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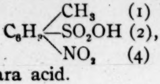
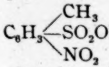
ON THE PREPARATION OF CERTAIN SULPHONIC ACIDS IN THE FREE STATE.

By J. H. Kastle.

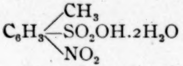
Our knowledge of strong acids is limited to a comparatively small group of substances. It is, therefore, a matter of some importance to devise methods whereby the number of such acids may be increased and our knowledge of them extended. The sulphonic acids furnish us with the largest class of strong acids known at present. Unfortunately, most of these can be obtained in the free condition only from their barium, lead or silver salts and this method is so tedious as ordinarily carried out that our knowledge of the acids in the free state is comparatively limited.

In the course of my investigations on this group of substances I have met with two members of the group of aromatic sulphonic acids which can be obtained in beautifully crystalline condition by the simplest possible methods. These two acids are *p*-nitrotoluenesulphonic acid,  $C_6H_3\begin{cases} CH_3 & (1) \\ SO_2OH & (2) \\ NO_2 & (4) \end{cases}$, and toluenesulphonic acid, probably the para acid.

The method employed in their isolation in the free condition depends upon the well-known chemical principle that substances containing a common ion show a diminished solubility in the presence of each other. Upon this principle depends the precipitation of sodium chloride from its aqueous solution by hydrochloric acid and the precipitation of sodium benzenesulphonate from its aqueous solutions by sodium chloride (Gattermann's method of obtaining sodium benzenesulphonate). In the same way certain of the sulphonic acids are precipitated from their concentrated aqueous solutions by another strong acid such as hydrochloric or sulphuric acid. Upon this principle depends the preparation of *p*-nitrotoluenesulphonic and toluenesulphonic acids in the free state.

p-*Nitrotoluenesulphonic Acid*,  $C_6H_3{<}\begin{array}{l}CH_3\\ SO_2OH.2H_2O\\ NO_2\end{array}$.—In order to prepare this acid, 50 grams of *p*-nitrotoluene are added to 200 grams of fuming sulphuric acid and the mixture heated on the water bath for a short time to complete the sulphonation. The mixture is then poured into 300 cc. of water and the mixture allowed to cool, when the whole liquid practically solidifies to a thick mass of crystals. This mixture of acid and crystals is then filtered on a platinum cone or a perforated porcelain funnel with the aid of the pump. There are thus obtained 120 grams of moist, granular crystalline acid having much the appearance of brown sugar. This can be recrystallized in the usual manner from hot water. After the third recrystallization the acid was found to contain small amounts of sulphuric acid. A saturated aqueous solution of *p*-nitrotoluenesulphonic acid, prepared as above described, is readily precipitated in the form of the dihydrate by means of concentrated hydrochloric acid. On the addition of an equal volume of concentrated hydrochloric acid to a concentrated aqueous solution of *p*-nitrotoluenesulphonic acid, the solution sets to a thick mass of pearly plates or scales, which, after filtration and drying in the air, have a soapy, unctious feel. After the second or third precipitation by means of concentrated hydrochloric acid, the acid was found to be free from sulphuric acid and on recrystallizing it from water by allowing the concentrated aqueous solution to slowly evaporate at ordinary temperatures the dihydrate was obtained in the form of beautiful, transparent, light yellow prisms of large size. These have been shown by one of my students in the Kentucky State University, Mr. C. W. Haynes, to contain two molecules of water of crystallization and not two and one-half molecules, as given by Jenssen.

The acid precipitated from its concentrated aqueous solution by concentrated hydrochloric acid is also the dihydrate, since 0.2532 gram of the acid required 0.0399 gram sodium hydroxide for neutralization; the calculated amount for



$C_6H_3\begin{matrix}CH_3\\SO_2OH.2H_2O\\NO_2\end{matrix}$ is 0.0400 gram.

In order, therefore, to obtain the dihydrate of *p*-nitrotoluenesulphonic acid in pure condition, sulphonate *p*-nitrotoluene with fuming sulphuric acid, pour the product of the sulphonation into about an equal volume of water, allow the mixture to cool, filter off the crystals on the pump and purify by solution in water, precipitation with concentrated hydrochloric acid and recrystallization of the product several times from water. For purposes of illustration and study this acid affords an excellent example of the whole group of aromatic sulphonic acids and even for the preparation of the salts and other derivatives of this acid it is a great saving of time to start with the acid prepared in this manner, rather than to prepare these substances from the calcium or barium salt, as is usually done.

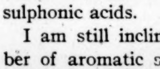
Toluenesulphonic Acid.—This acid may be obtained in the free condition in precisely the same way as the *p*-nitrotoluenesulphonic acid. It was prepared by adding 100 cc. of toluene in small amounts at a time to 200 cc. of commercial sulphuric acid, sp. gr. 1.84, with constant shaking. When the toluene had all dissolved the mixture was poured into 120 cc. of water and the mixture allowed to cool. Large prismatic crystals of toluenesulphonic acid (probably the para acid), some of them one to two inches in length, separate on cooling. The yield is practically quantitative. A quantity of these crystals was dissolved in the smallest possible amount of warm water. On cooling a considerable amount of the acid again separated in the form of prismatic crystals. These were filtered off and the filtrate, which was saturated with the toluenesulphonic acid at ordinary temperature, was divided into two parts of 55 cc. each To one of these portions was added 100 cc. of concentrated hydrochloric acid and to the other 50 cc. In both cases the solution instantly set to a thick paste of crystals. These solutions containing the crystals were then heated, when the crystals dissolved, and on allowing the solutions to stand overnight good crops of large crystals of the toluenesulphonic acid were obtained. These were filtered off and were found to contain small amounts of sulphuric acid, and after drying in a desiccator over solid caustic soda, overnight, they showed traces of hydrochloric acid with silver nitrate. They were then dissolved in the smallest possible amount of water, two volumes of concentrated hydrochloric acid added and the paste of crystals thus obtained dissolved by warming. The solution thus obtained was again allowed to stand overnight when aggregates of large, colorless prismatic crystals, many of them one to one and a half inches in length, separated from the solution. These were found to be free from sulphuric acid. After drying in a desiccator over solid caustic soda for two months these crystals appeared to be absolutely dry, but still were found to contain traces of hydrochloric acid. It would seem, therefore, that the last traces of free hydrochloric acid can be removed only by recrystallization from water. The toluenesulphonic acid obtained by this method appears to be a monohydrate. Thus 0.7160 gram of the acid which had stood two months over solid caustic soda required 0.1521 gram sodium hydroxide for neutralization. For the monohydrate 0.1506 gram would be required, whereas the anhydrous acid would require 0.1664, and the dihydrate 0.1376 gram. It is evident also that the single molecule of water of crystallization which this hydrate contains cannot be removed by drying over solid caustic soda. It is more than likely that the acid with which we are here dealing is the para compound. This, however, has not as yet been proven experimentally. One would certainly be inclined to believe *a priori*, I think, that the method above described for the isolation of these two sulphonic acids would be a general one for the entire group of aromatic sulphonic acids. Such, however, has unfortunately not proven to be the case. For example, I have failed to isolate benzenesulphonic and *o*-nitrotoluenesulphonic acids by this method. Thus when the product of the sulphonation of benzene, resulting from heating benzene for several days with commercial sulphuric acid, under a reflux condenser, was mixed with water in the proportion of 0.5, 1, 2, 3 and 4 volumes of water to 1 volume of the acid mixture, there was no formation of any crystals even after long standing, and all of my experiments with *o*-nitrotoluenesulphonic acid have resulted negatively. The failure to obtain these acids is doubtless due to a greater solubility of these two acids in sulphuric acid, dilute and concentrated, than holds for toluenesulphonic and *p*-nitrotoluenesulphonic acids.

I am still inclined to believe, however, that a large number of aromatic sulphonic acids can be isolated in the free condition by this method. The fact that *p*-nitrotoluenesulphonic acid can be obtained so easily and that in the form of the dihydrate is such a well-defined chemical species opens up a number of new lines of investigation on the solubility of this acid in various acid mixtures which, with the aid of my students, I hope to follow as soon as the opportunity presents itself.

University of Virginia,
September, 1910.

SEVERAL ACIDS SUITABLE FOR USE AS STANDARDS IN ACIDIMETRY.

By J. H. Kastle.

In view of the fact that *p*-nitrotoluenesulphonic acid,  $C_6H_3\begin{cases}CH_3 & (1)\\ SO_2OH & (2)\\ NO_2 & (4)\end{cases}$, is completely ionized in aqueous solution and in view of the ease with which it may be obtained in a beautifully crystalline condition, it occurred to the writer that possibly it could be used to advantage as a standard in acidimetry.

I, therefore, suggested to one of my students in the Kentucky State University, Mr. Haynes,[1] that he undertake an investigation of this acid with this object in view. Accordingly he prepared a standard solution of sodium hydroxide, containing 5.66 milligrams per cc., by titration against a standard solution of sulphuric acid, the exact concentration of which had been determined gravimetrically in the usual manner. Weighed amounts of *p*-nitrotoluenesulphonic acid, which had been carefully purified by several crystallizations from water,[2] were then titrated with this standard solution of sodium hydroxide, using phenolphthalein as the indicator, with the following results:

Quantity of acid used, in grams.	Sodium hydroxide required, in cc.	Milligrams of sodium hydroxide per cc.
0.2000	5.61	5.632
0.3000	8.40	5.642
0.2998	8.38	5.653
0.6535	18.26	5.654
0.3993	11.15	5.658
0.3637	10.14	5.666
0.2172	6.08	5.643
Total, 2.4335	68.02	39.548
	Average,	5.65

Hence, according to his findings, 1 gram of *p*-nitrotoluenesulphonic acid requires 0.1582 gram of sodium hydroxide for neutralization; the calculated amount is 0.1580 gram.

During the course of this investigation Mr. Haynes observed that, as ordinarily obtained by precipitation from its solutions in fuming sulphuric acid by water and recrystallization from water, *p*-nitrotoluenesulphonic acid contains two molecules of water of crystallization and not two and one-half molecules as found by Jenssen.[3] Thus he found that on drying at 125° to 130° C., 0.3370 gram of the hydrated acid lost 0.0485 gram (14.39 per cent.) and that when heated again for half an hour at this temperature there was no further loss of weight. In another experiment he found that 0.4000 gram of the hydrated acid gradually lost, on heating for seven hours at 123° to 131°, 0.0570 gram (14.25 per cent.) and that on heating one hour longer it suffered no further loss of weight. The calculated value for two molecules of water is 14.23 per cent., whereas for two and one-half molecules it is 17.17 per cent. It follows, therefore, that the modification of the acid with which we were dealing was the dihydrate. Obviously the results of Mr. Haynes's titrations of this acid with standard sodium hydroxide are also in harmony with this conclusion. About this time, *viz.*, 1905, my chemical work was diverted somewhat from its usual channels with the result that these observations made by Mr. Haynes, while working under my direction, were never published.

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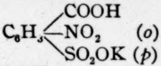
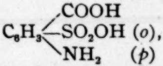
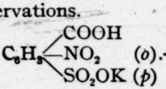
[1] "Some Methods of Standardizing Acid and Alkali Solutions." Thesis for the degree of Bachelor of Science in Chemistry, by C. W. Haynes, State College of Kentucky, 1905.

[2] For details concerning the preparation of *p*-nitrotoluenesulphonic acid, see the preceding paper.

[3] Ann. Chem. (Liebig), **172**, 230.

My attention has again been directed to the subject, however, by reason of the fact that in the course of certain investigations now being carried out in this laboratory I have recently had occasion to prepare and examine two other acids which possess in high degree those characteristics required of standards for use in acidimetry. These are the monopotassium salt of *o*-nitro-*p*-sulphobenzoic acid,  $C_6H_3\left<\begin{matrix}COOH \\ NO_2\ (o) \\ SO_2OK\ (p)\end{matrix}\right.$, and *p*-amino-*o*-sulphobenzoic acid,  $C_6H_3\left<\begin{matrix}COOH \\ SO_2OH\ (o) \\ NH_2\ (p)\end{matrix}\right.$, both of which were first obtained by Hart[1] in the course of an experimental study of the nitrosulphobenzoic acids and some of their derivatives. I have, therefore, deemed it advisable to propose these two acids as standards in acidimetry and to include a few determinations of my own on *p*-nitrotoluenesulphonic acid, in addition to the results obtained by Mr. Haynes, as given above. For the preparation of these two compounds, I have made use of the following methods, based for the most part on Hart's original observations.

Monopotassium o-*Nitro*-p-*sulphobenzoate*,  $C_6H_3\left<\begin{matrix}COOH \\ NO_2\ (o) \\ SO_2OK\ (p)\end{matrix}\right.$.—

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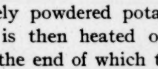
[1] This Journal, 1, 340–356 (1879–80).

In order to prepare this compound, *o*-nitrotoluene is sulphonated by adding it gradually to fuming sulphuric acid, in the proportion of one or two volumes of acid to every volume of *o*-nitrotoluene used, and heating the mixture on the water bath for a few minutes to complete the sulphonation. The mixture is then largely diluted with water, heated nearly to boiling, neutralized with chalk and filtered while hot from the calcium sulphate. The calcium in the hot filtrate is then exactly precipitated with potassium carbonate and the calcium carbonate removed by filtration. The filtrate containing the potassium salt of *o*-nitro-*p*-toluenesulphonic acid is then evaporated to crystallization. On cooling this salt separates in needle-shaped crystals or in pearly, lustrous scales. This salt is then converted into the potassium salt of *o*-nitro-*p*-sulphobenzoic acid by oxidizing with potassium permanganate in alkaline solution. Ten parts by weight of the potassium salt of *o*-nitro-*p*-toluenesulphonic acid and 3 parts by weight of potassium hydroxide are dissolved in 500 parts of water. This solution is then heated on the water bath and 22 parts by weight of finely powdered potassium permanganate added. The mixture is then heated on the water bath for eight to ten hours, at the end of which time a small amount of alcohol is added to decompose any permanganate remaining unchanged. The mixture is then filtered and the clear golden yellow filtrate evaporated to small bulk, when it is allowed to cool and then strongly acidified with concentrated hydrochloric acid. The acid potassium salt of *o*-nitro-*p*-sulphobenzoic acid is thus obtained in the form of anhydrous, prismatic plates which are purified by crystallization from hot water, after the addition of animal charcoal. The salt employed in this investigation was beautifully crystalline, highly refractive, transparent, white to very slightly yellowish and on pulverization yielded a white powder. On heating for one hour in the air bath at 130°–158° the salt showed no loss of weight. It is therefore anhydrous and was so described by Hart.

p-*Amino*-o-*sulphobenzoic Acid*,



$C_6H_3\begin{cases}COOH \\ SO_2OH\ (o) \\ NH_2\ (p)\end{cases}$.—The starting point in the preparation of this acid is the acid potassium salt of *p*-nitro-*o*-sulphobenzoic acid, $C_6H_3\begin{cases}COOH \\ SO_2OK\ (o) \\ NO_2\ \ (p)\end{cases}$. H_2O, which in turn is obtained from *p*-nitrotoluene by sulphonation with fuming sulphuric acid and oxidation with alkaline permanganate according to the directions given by Hart[1] and Kastle.[2] In order to obtain the *p*-amino-*o*-sulphobenzoic acid, the acid potassium salt of *p*-nitro-*o*-sulphobenzoic acid prepared according to Kastle's directions is dissolved in a considerable excess of strong ammonia and the solution saturated with hydrogen sulphide. The solution is then evaporated to dryness on the water bath and the residue is extracted with a small amount of hot water and filtered to remove the sulphur. Hydrochloric acid is then added to the filtrate, when the *p*-amino-*o*-sulphobenzoic acid separates on cooling in the form of delicate, white needles, which are anhydrous. The compound can be purified by crystallization from boiling water containing animal charcoal.

The quantities of sodium hydroxide required to neutralize known amounts of these two compounds and of *p*-nitrotoluenesulphonic acid were then determined in the following manner. Approximately 0.1 N solutions of hydrochloric acid and sodium hydroxide were prepared; 50 cc. of the solution of hydrochloric acid required 50.5 cc. of the solution of sodium hydroxide for neutralization, phenolphthalein being used as the indicator. Duplicate gravimetric determinations of the amount of hydrochloric acid in 50 cc. portions of the solution gave 0.7261 and 0.7259 gram silver chloride, respectively.

Hence, 1 cc. of the solution of hydrochloric acid contains 0.00369412 gram acid and 1 cc. of the solution of sodium hydroxide contains 0.00401258 gram base. Weighed amounts of the three acids here under investigation, the *p*-nitrotoluenesulphonic acid air-dried, the other two, first air-dried and then dried for an hour at 110° in the air bath, were then dissolved in water and titrated with the solution of sodium hydroxide, phenolphthalein being used as the indicator, with the following results:

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[1] *Loc. cit.*, pp. 349–352.

[2] THIS JOURNAL, **11**, 179 (1889).

Acid.	Quantity of acid taken, in grams.	Sodium hydroxide required for neutralization, in cc.	0.1 N Sodium hydroxide required for neutralization, in cc. (Calc., 50)	Quantity of sodium hydroxide found to be required for neutralization, in grams. (Calc., 0.20004)
p-Nitrotoluenesulphonic	1.2658	49.95	50.097	0.200428
p-Amino-*o*-sulphobenzoic	0.5428	49.85	49.997	0.200027
Monopotassium *o*-nitro-*p*-sulphobenzoate	1.4260	50.00	50.147	0.200629

The several quantities of sodium hydroxide required to neutralize 1 gram of each of these acids, together with the calculated amounts, are as follows:

	Sodium hydroxide required to neutralize 1 gram of acid, in grams.	
Acid.	Found.	Calculated.
p-Nitrotoluenesulphonic	0.1582 (Haynes) 0.1583 (Kastle)	0.15803
p-Amino-*o*-sulphobenzoic	0.36851	0.36853
Monopotassium *o*-nitro-*p*-sulphobenzoate	0.1407	0.14028

For all practical purposes, and it is only for such purposes that these standard acids are recommended, the slight differences between the found and calculated values of the several amounts of sodium hydroxide required to neutralize these three acids are of no significance and in the case of one of them at least, *viz.*, the *p*-amino-*o*-sulphobenzoic acid, the agreement is such as to meet the most exact requirements of volumetric analysis.

To review briefly the properties which render these compounds of value as standards in acidimetry: We see that each of them is a very definite and well-defined chemical species. They are all easily prepared and are readily obtained in perfectly pure condition. Two of them, *viz.*, *p*-amino-*o*-sulphobenzoic acid and monopotassium *o*-nitro-*p*-sulphobenzoate are anhydrous and, hence, can be thoroughly dried in the air and also by the aid of heat or in the desiccator over sulphuric acid, without danger of alteration in composition. All of them are stable in the air under ordinary conditions, none of them are hygroscopic or deliquescent. All of them give very sharp end reactions with phenolphthalein, one drop of 0.1 N sodium hydroxide being sufficient to change the color of the titer from colorless to pink. As shown by Mr. Haynes, *p*-nitrotoluenesulphonic acid crystallizes with two molecules of water of crystallization. It is obviously open to the objections which have been urged against all hydrates as chemical standards, such as danger of occluded mother liquor, difficulty of drying without loss of water of hydration, etc. On the other hand, this particular compound is very definite and stable under ordinary atmospheric conditions, showing great tendency to crystallize. It is completely ionized at ordinary dilutions.

Its reaction towards indicators is particularly sharp and definite, so that in my opinion it has much to commend it as a standard in acidimetry, despite the fact that it is hydrated.

UNIVERSITY OF VIRGINIA,
August, 1910.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXXVI.—ON IODINE DERIVATIVES OF TOLUENE.

BY HENRY L. WHEELER.

EXPERIMENTAL WORK BY CHARLES A. BRAUTLECHT AND CHARLES HOFFMAN.

There are nineteen nucleus-substituted iodine derivatives of toluene: three mono-, six di-, six tri-, three tetra- and one pentaiodtoluenes.

When the work on iodtoluenes was started in this laboratory only two of these polyiod derivatives of known structure had been described. 2,6-Diiodtoluene had been prepared by Cohen and Miller[1] from the corresponding iodnitrotoluene and 3,4-diiodtoluene had been obtained by Willgerodt and Simonis.[2]

Neumann[3] found that when *o*- or *p*-iodtoluene was heated with sulphuric acid a di- and a triiodtoluene were formed. For no reason, otherwise than that he started with an *o*- or *p*-iodtoluene, these products were considered to have iodine atoms in these positions and to be 2,4-diiod- and 2,4,6-triiodtoluenes.

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[1] J. Chem. Soc., **85**, 1627 (1904).

[2] Ber. d. chem. Ges., **39**, 269 (1906).

[3] Ann. Chem. (Liebig), **241**, 50 (1887).

We have prepared 2,4-diiodtoluene from 2,4-dinitrotoluene by alternately reducing the nitro groups and replacing the amino groups by iodine. We obtained an oil with the properties described by Neumann; his assumption was therefore correct in this case. Ortho- and metaiodtoluenes are the only other members of this series that are oils at ordinary temperature.

In regard to the triiodtoluene, which was prepared according to his directions, it was noticed that the substance has the same melting point (118°–119°) as 2,4,5-triiodtoluene, and this triiodtoluene we have prepared by three different methods. When the substances were mixed the melting point was not altered. On the other hand, when Neumann's triiodtoluene was mixed with 2,4,6-triiodtoluene, prepared from 2,4,6-triiod-*m*-toluidine, the mixture melted at 75°–85°. The triiodtoluene in question is therefore 2,4,5- and not 2,4,6-triiodtoluene.

2,4-Dichlor- and 2,4,5-trichlortoluenes are the main products formed on chlorinating toluene.[1]

In our paper on the action of iodine on *p*-toluidine we described 2,3-diiodtoluene, 3,5-diiodtoluene and 3,4,5-triiodtoluene[2] and our article on the action of iodine on *o*-toluidine contained a description of 2,5,-diiodtoluene,[3] while the investigation of the action of iodine on *m*-toluidine led to the preparation of 2,3,6-triiodtoluene, 3,4,6-triiodtoluene and 2,3,4,6-tetraiodtoluene.[4]

In this paper we describe the remaining nucleus-substituted iodine derivatives of toluene required by theory. The methods used for their preparation were as follows: We found that

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[1] Cohen and Dakin: J. Chem. Soc., **81**, 1340 (1902).

[2] This Journal, **42**, 441 (1909).

[3] *Ibid.*, **42**, 498

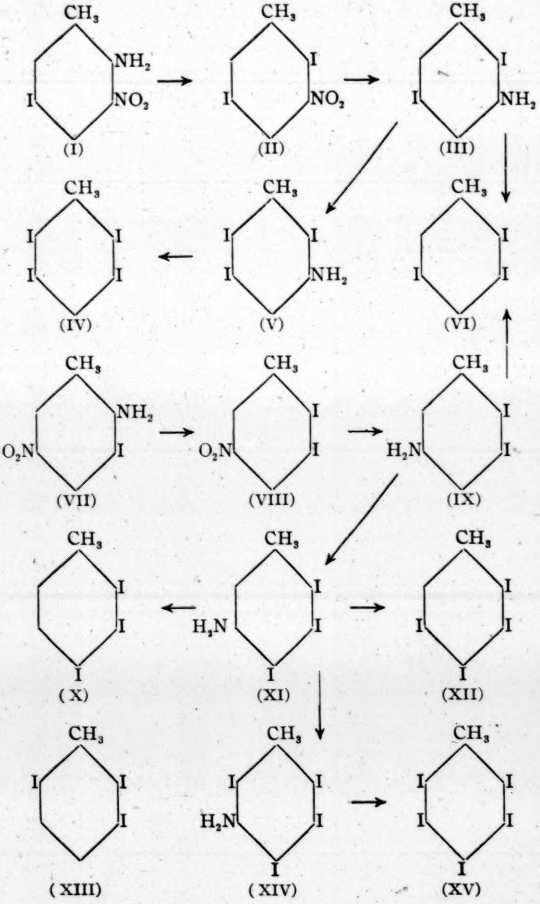
[4] *Ibid.*, **44**, 126 (1910).

3-nitro-*o*-toluidine is attacked by iodine monochloride in the 5-position, giving 5-iod-3-nitro-*o*-toluidine (I), while 5-nitro-*o*-toluidine gives 3-iod-5-nitro-*o*-toluidine (VII). This was shown by replacing the amino groups in these compounds by iodine. The resulting 2,5-diiod-3-nitrotoluene (II) and 5,6-diiod-3-nitrotoluene (VIII) were reduced to 2,5-diiod-*m*-toluidine (III) and 5,6-diiod-*m*-toluidine (IX). Then by means of the diazo reaction a triiodtoluene melting at 72°–73° was obtained from both of these toluidines. Since the products obtained by these two methods proved to be identical, and this compound was not identical with 2,3,6-triiodtoluene (XIII), melting at 80°.5, it was therefore 2,3,5-triiodtoluene (VI).

When 5,6-diiod-*m*-toluidine (IX) was treated with iodine the hydrogen in the 4-position was first substituted. This was shown on removing the amino group from the triiodtoluidine (XI) thus formed, whereupon a triiodtoluene (X), melting at 92°, was obtained. This was different from 2,3,6-triiodtoluene (XIII) from 2,6-diiod-*m*-toluidine. This 2,3,6-triiodtoluene would result if the substitution in 5,6-diiod-*m*-toluidine took place in the 2-position. The triiodtoluene obtained in this case was therefore 2,3,4-triiodtoluene (X).

On this fact is also based the structure of 2,3,4,5-tetraiodtoluene (XII) prepared from the triiodtoluidine (XI) by replacing the amino group by iodine, and, since by the action of iodine on 2,5-diiod-*m*-toluidine (III) a triiod-*m*-toluidine (V) results, which gives a different tetraiodtoluene (IV), it follows that 2,5-diiod-*m*-toluidine (III) is attacked in the 6-position or para to the amino group, the product in this case being 2,5,6-triiod-*m*-toluidine (V), and the tetra derivative from this is 2,3,5,6-tetraiodtoluene (IV).

Both 4,5,6-triiod-*m*-toluidine (XI) and 2,5,6-triiod-*m*-toluidine (V) are further acted on by iodine and a tetraiodtoluene is formed. The products in these two cases were identical, as required by theory, and when the amino group in this compound was diazotized and replaced by iodine pentaiodtoluene (XV) was obtained.


CH$_3$
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NO$_2$
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(XIV)
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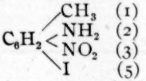
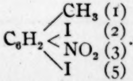
H$_2$N
O$_2$N



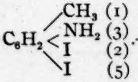
5-Iod-3-nitro-o-toluidine, $C_6H_2<\begin{matrix}CH_3 & (1)\\ NH_2 & (2)\\ NO_2 & (3)\\ I & (5)\end{matrix}$.—3-Nitro-*o*-toluidine was prepared by nitrating *o*-acettoluide in the manner described by Reverdin and Crépieux.[1] Twenty-two and a half grams of this compound were suspended in 20 grams of glacial acetic acid and 24.5 grams of iodine monochloride were added. The reaction takes place with evolution of heat but nevertheless the mixture was warmed to boiling for a few minutes. It was then treated with dilute sodium hydroxide and hot water. The yield of crude 5-iod-3-nitro-*o*-toluidine was 39.7 grams or 98 per cent. of the calculated. It crystallized from alcohol in orange needles melting at 135°. It is difficultly soluble in water and easily in hot alcohol.

	Calculated for $C_7H_7O_2N_2I$.	Found. I.	Found. II.
N	10.07	9.88	10.03



2,5-Diiod-3-nitrotoluene, $C_6H_2<\begin{matrix}CH_3 & (1)\\ I & (2)\\ NO_2 & (3)\\ I & (5)\end{matrix}$.—5-Iod-3-nitro-*o*-toluidine was mixed with 4 parts of concentrated sulphuric acid, cooled in a freezing mixture, and a half part of dry powdered sodium nitrite added. When the whole was poured on cracked ice, an almost complete solution resulted. The filtered diazo solution was then treated with 3.5 parts of potassium iodide dissolved in a little ice water. The yield of crude diiodnitrotoluene obtained on warming the solution, averaged, as the result of seven experiments, about 81 per cent. of the calculated. When the material was crystallized from alcohol we obtained colorless prisms melting, to an oil, at 95°.

	Calculated for $C_7H_5O_2NI_2$.	Found. I.	Found. II.
N	3.60	3.49	3.52



*2,5-Diiod-*m*-toluidine*, $C_6H_2<\begin{matrix}CH_3 & (1)\\ NH_2 & (3)\\ I & (2)\\ I & (5)\end{matrix}$.—One part of 2,5-diiod-3-nitrotoluene was reduced by warming for several hours with a mixture of 8 parts hydrated ferrous sulphate and 20 parts of concentrated ammonium hydroxide diluted with 8–20 parts of water. On filtering and extracting the residue with alcohol the yield of crude material was usually about 60 per cent. of the calculated. When crystallized from alcohol, after boiling with animal charcoal, pale brown prisms, melting at 82°, were obtained.

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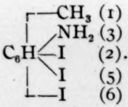
[1] Ber. d. chem. Ges., **33**, 2498.

	Calculated for $C_7H_7NI_2$.	Found.
I	70.75	70.62

When this substance was diazotized and the solution treated with potassium iodide, in the usual manner, the product crystallized from alcohol in buff-colored plates. They melted at 72°–73° and proved to be identical with 3,5,6- (or 2,3,5-) triiodtoluene prepared by Hoffman from 5,6-diiod-*m*-toluidine (see below). This fact has served to determine the structure of this and the related iodine derivatives. This triiodtoluene is practically nonvolatile in steam. Two and a half liters of distillate contained about 0.05 gram.

*2,5-Diiod-*m*-acettoluide*, $C_6H_2CH_3I_2NHCOCH_3$, from the base and acetic anhydride, crystallized from alcohol, in which it is moderately soluble, in long, colorless, feltlike needles, melting at 198°–199°. It is practically insoluble in water.

	Calculated for $C_9H_9ONI_2$.	Found.
N	3.49	3.47

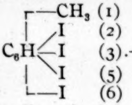
*2,5,6-Triiod-*m*-toluidine*, 

$$C_6H\left\{\begin{array}{ll}-CH_3 & (1)\\ NH_2 & (3)\\ -I & (2)\\ I & (5)\\ -I & (6)\end{array}\right.$$

—Seven grams of 2,5-diiod-*m*-toluidine, 5 grams of iodine, 4 grams of calcium carbonate, 20 cc. of ether and 15 cc. of water were warmed on the steam bath for 18 hours. The ether was evaporated, the solution filtered and the residue extracted with alcohol; on concentrating the alcoholic solution about 50 per cent. of the calculated amount of triiod-*m*-toluidine separated. When crystallized from alcohol it formed colorless needles which melted sharply at 119°–120°.

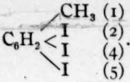
	Calculated for $C_7H_6NI_3$.	Found.
N	2.89	2.87

When four atomic proportions of iodine were used in the above experiment 10 grams of 2,5-diiod-*m*-toluidine gave a mixture of about equal parts of 2,5,6-triiod-*m*-toluidine and 2,4,5,6-tetraiod-*m*-toluidine, melting at 205° and described by Hoffman below. The compounds were obtained by first extracting with alcohol, then with acetic acid or benzene.

2,3,5,6-Tetraiodtoluene,  $C_6H\left\{\begin{array}{ll} CH_3 & (1)\\ I & (2)\\ I & (3)\\ I & (5)\\ I & (6)\end{array}\right.$.—When the above 2,5,6-triiod-*m*-toluidine was diazotized in the usual manner, a noticeable quantity of material remained undissolved. On treating the clear diazo solution with potassium iodide the yield, in two experiments, was 64 per cent. of the calculated. The product was crystallized from benzene; it then formed colorless, arborescent needles melting to a clear oil at 125°. It was less soluble in alcohol than in benzene.

	Calculated for $C_7H_4I_4$.	Found.
I	85.23	84.53

Since this tetraiodtoluene is different from the tetraiodtoluene (melting at 284°) obtained by Hoffman (below) from 4,5,6-triiod-*m*-toluidine, it follows that this must be the 2,3,5,6-derivative and that 2,5-diiod-*m*-toluidine iodates in the 6-position or para to the amino group, otherwise the two methods should yield the same tetraiodtoluene.

2,4,5-Triiodtoluene,  $C_6H_2<\begin{array}{ll} CH_3 & (1)\\ I & (2)\\ I & (4)\\ I & (5)\end{array}$.—This substance, which may be considered as 3,4,6-triiodtoluene, was described in one of our previous papers.[1] It was prepared from 4,6-diiod-*m*-toluidine. We have now prepared the same substance in two other ways, namely from *p*-iod-*o*-toluidine and from *p*-nitro-*o*-toluidine.

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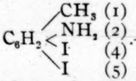
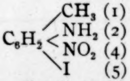
[1] THIS JOURNAL, **44**, 140 (1910).



4,5-Diiod-o-toluidine, $C_6H_2<\begin{array}{ll}CH_3 & (1)\\ NH_2 & (2)\\ I & (4)\\ I & (5)\end{array}$.—This was obtained by the action of iodine, or better by the action of iodine monochloride, on *p*-iod-*o*-toluidine in glacial acetic acid. After adding water and then washing the precipitate with dilute alkali it crystallized from alcohol in stout needles or long, colorless prisms. It melted constantly at 85°.

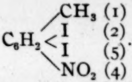
	Calculated for $C_7H_7NI_2$.	Found.
N	3.90	3.86

When this material was diazotized in the usual manner and the solution treated with potassium iodide, the triiodtoluene obtained, after crystallizing from alcohol, melted at 118°–119°, and when mixed with 3,4,6-triiodtoluene the melting point was not lowered.



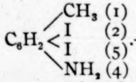
4-Nitro-5-iod-o-toluidine, $C_6H_2<\begin{array}{ll}CH_3 & (1)\\ NH_2 & (2)\\ NO_2 & (4)\\ I & (5)\end{array}$.—Fourteen grams of *p*-nitro-*o*-toluidine were dissolved in glacial acetic acid and allowed to stand for 3 days with 15 grams of iodine monochloride. The crystals which separated were dissolved in water containing a little hydrochloric acid and the solution was poured into aqueous ammonia. Long, bright yellow prisms separated, which, when crystallized from alcohol, melted at 109°. The yield in this experiment was 70 per cent. of the calculated, in others more or less tar was formed.

	Calculated for $C_7H_7O_2N_2I$.	Found.
N	10.07	9.87



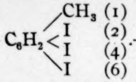
2,5-Diiod-4-nitrotoluene, $C_6H_2<\begin{array}{ll}CH_3 & (1)\\ I & (2)\\ I & (5)\\ NO_2 & (4)\end{array}$.—Eighteen grams of 4-nitro-5-iod-*o*-toluidine were diazotized and the solution treated with potassium iodide in excess. This gave 20 grams of diiodnitrotoluene which, when crystallized from alcohol, in which it is moderately soluble, formed buff-colored prismatic plates, melting sharply at 117°.

	Calculated for $C_7H_5O_2NI_2$.	Found.
N	3.60	3.57

2,5-Diiod-p-*toluidine*,  $C_6H_2<\begin{matrix}CH_3 & (1)\\ I & (2)\\ I & (5)\\ NH_2 & (4)\end{matrix}$.—Ten grams of the above nitro compound were reduced with ferrous sulphate and ammonia in the usual manner. The product was extracted with alcohol and on concentrating and cooling the solution 6 grams of buff-colored prisms were obtained. On recrystallizing from alcohol they melted constantly at 109°.

	Calculated for $C_7H_7NI_2$.	Found.	
		I.	II.
N	3.90	3.64	3.84

When this substance was diazotized and treated with potassium iodide 2,4,5-triiodtoluene was obtained. This triiodtoluene is identical with the one obtained by Neumann[1] by warming *o*- or *p*-iodtoluene with sulphuric acid.

2,4,6-Triiodtoluene,  $C_6H_2<\begin{matrix}CH_3 & (1)\\ I & (2)\\ I & (4)\\ I & (6)\end{matrix}$.—Neumann's supposed 2,4,6-triiodtoluene was prepared from *p*-iodtoluene according to his directions. It melted at 118° and when mixed with 2,4,5-triiodtoluene, prepared by the three different methods given above, the melting point was not lowered. When it was mixed with the true 2,4,6-triiodtoluene from 2,4,6-triiod-*m*-toluidine the mixture melted as low as 75°–85°. The triiodtoluene prepared by Neumann's method is colorless or has a pale cream color. 2,4,5-Triiodtoluene prepared by our methods has a brownish white color which can be removed by boiling the alcoholic solution with animal charcoal.

Eight and eight-tenths grams of 2,4,6-triiod-*m*-toluidine were dissolved in 30 cc. of concentrated sulphuric acid and cooled in a freezing mixture. To the purple solution 5 grams of dry, powdered sodium nitrite were added and the mixture poured upon crushed ice. After standing for a half hour a lemon-colored diazo solution and a bright yellow residue were obtained. The solution was poured into 100 cc. of alcohol and allowed to stand for an hour, then boiled for another hour. Light brown crystalline material separated and when this was filtered off and dried it weighed 2.6 grams, or 31 per cent. of the calculated. It was readily soluble in benzene from which it crystallized in colorless needles. It was difficultly soluble in alcohol and it melted to a clear oil at 105°.

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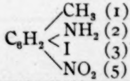
[1] Ann. Chem. (Liebig), **240**, 50.

	Calculated for $C_7H_5I_3$.	Found.
I	81.06	80.49

When the yellow residue which was obtained above was dissolved in sulphuric acid, diazotized a second time, and the solution treated with alcohol, a further quantity (20 per cent. of the calculated) of triiodtoluene was obtained.

By Charles Hoffman.

*3-Iod-5-nitro-*o*-toluidine,*  $C_6H_2 < \begin{matrix} CH_3 & (1) \\ NH_2 & (2) \\ I & (3) \\ NO_2 & (5) \end{matrix}$.—Eight grams of 5-nitro-*o*-toluidine[1] were dissolved in 55 cc. of glacial acetic acid and to this solution 13 grams of iodine monochloride (1 mol.) were slowly added, with constant shaking. The mixture became warm and a brown precipitate soon separated after all the monochloride was added. The mixture was then heated for an hour under a return condenser. A solution of acid sodium sulphite was added and the solid substance which separated was filtered, washed and dried. The yield was 13.7 grams, or 90 per cent. of the calculated. The crude product melted at 171° and when crystallized twice from alcohol it gave long, brown prisms, melting to a clear oil at 173°. The material was insoluble in water, alkali and dilute acids, but readily soluble in alcohol and benzene. The action of 2 molecular proportions of iodine monochloride on 5-nitro-*o*-toluidine gave the same compound.

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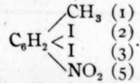
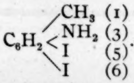
[1] Reverdin and Crépieux: Ber. d. chem. Ges., **33**, 2498.

	Calculated for $C_7H_7O_2N_2I$.	Found.
N	10.08	10.24



2,3-Diiod-5-nitrotoluene, $C_6H_2{<}\begin{matrix}CH_3 & (1)\\ I & (2)\\ I & (3)\\ NO_2 & (5)\end{matrix}$.—Five grams of 3-iod-5-nitro-*o*-toluidine were dissolved in 10 cc. of cold, concentrated sulphuric acid and to this solution 2.5 grams of finely powdered dry sodium nitrite were added at 0°. The brown, pasty mixture was poured on finely crushed ice, whereupon a light brown solution was obtained. The diazo solution, after standing a half hour, was filtered from a small amount of undissolved material into a flask containing an ice-cold solution of 20 grams of potassium iodide. A brownish-red diazo iodide separated which decomposed upon heating, giving off nitrogen. The dark substance, containing iodine, was decolorized by means of acid sodium sulphite. The crude product then weighed 6.4 grams, or 93 per cent. of the calculated. From alcohol it formed long, prismatic, light brown needles and it melted to an oil at 143°. It is moderately soluble in hot alcohol, readily soluble in cold benzene, difficultly soluble in petroleum ether and water.

	Calculated for $C_7H_5O_2NI_2$.	Found.
N	3.60	3.53

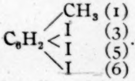


5,6-Diiod-m-toluidine, $C_6H_2{<}\begin{matrix}CH_3 & (1)\\ NH_2 & (3)\\ I & (5)\\ I & (6)\end{matrix}$.—Twenty-five grams of the above 2,3-diiod-5-nitrotoluene or 5,6-diiod-3-nitrotoluene, 180 grams of ferrous sulphate (10 molecules), 500 cc. of water and 250 cc. of concentrated ammonia were mixed and allowed to stand for 15 hours at 60°. The mixture was then filtered and the residue extracted with alcohol. This gave 14.3 grams of material melting at 105°–106°, which is 62 per cent. of the calculated. Two crystallizations from alcohol produced large, brown, spikelike crystals which melted to an oil at 106°. This compound distilled slowly with steam; it was then obtained colorless, and the melting point was not changed. It is readily soluble in alcohol and difficultly in petroleum ether and water. With mineral acids it forms salts which are difficultly soluble.

	Calculated for $C_7H_7NI_2$.	Found.
I	70.75	70.77

5,6-Diiod-m-*acettoluide*, $C_6H_2I_2CH_3NHCOCH_3$, from the base and acetic anhydride, crystallizes from alcohol in small, spike-like clusters of crystals melting at 208°. It is moderately soluble in alcohol and difficultly soluble in hot water.

	Calculated for $C_9H_9ONI_2$.	Found.
N	3.49	3.38

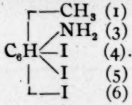
3,5,6-Triiodtoluene, 

$$C_6H_2\left\langle\begin{array}{ll} CH_3 & (1)\\ I & (3)\\ I & (5)\\ I & (6)\end{array}\right.$$

.—This was prepared from 5,6-diiod-*m*-toluidine by diazotizing and treating the solution with potassium iodide as described in the case of 2,3-diiod-5-nitrotoluene. 5,6-Diod-*m*-toluidine, like 4,6-diiod-*m*-toluidine, forms a very difficultly soluble sulphate which it is difficult to diazotize by the above method. The sulphuric acid solution of 5 grams of the base, containing an excess of nitrite, after being poured on crushed ice, was allowed to stand for 1 hour, then filtered from unaltered sulphate. The weight of triiodtoluene obtained was 3.5 grams, or 53 per cent. of the calculated. When the material was crystallized from alcohol it formed large, light orange, twinned plates, melting at 72°-73°.

	Calculated for $C_7H_5I_3$.	Found.
I	81.06	80.30

This compound, which may also be considered as 2,3,5-triiodtoluene, is identical with the triiodtoluene from 2,5-diiod-*m*-toluidine (Brautlecht). When the different preparations were mixed the melting point was not altered.

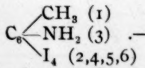
4,5,6-Triiod-m-*toluidine*, 

$$C_6H\left\{\begin{array}{ll} CH_3 & (1)\\ NH_2 & (3)\\ I & (4)\\ I & (5)\\ I & (6)\end{array}\right.$$

.—Five grams of 5,6-

diiod-*m*-toluidine were mixed with two molecular proportions of iodine (I_4) in the presence of some water, ether and an excess of calcium carbonate. The mixture was warmed on the steam bath under a return condenser for 35 hours. Steam was then passed in until the free iodine was removed. No unaltered diiod-*m*-toluidine distilled over. The substance left in the flask was filtered and the residue was extracted with alcohol. This treatment gave 3 grams of material melting at 118°–120°, which, as triiod-*m*-toluidine, corresponds to 45 per cent. of the diiod-*m*-toluidine. Several crystallizations from alcohol, in which the substance is readily soluble, gave small, brown needles, melting constantly, to a clear oil, at 122°. This base dissolves to only a slight extent in dilute hydrochloric acid.

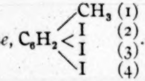
	Calculated for $C_7H_6NI_3$.	Found.	
		I.	II.
N	2.89	2.85	2.75

2,4,5,6-Tetraiod-m-*toluidine*,  $C_6\begin{cases}CH_3\ (1)\\ NH_2\ (3)\\ I_4\ (2,4,5,6)\end{cases}$.—The residue remaining from the above, after three or four extractions with alcohol, was treated with dilute hydrochloric acid to dissolve the calcium carbonate. The residue remaining was filtered and then extracted with glacial acetic acid. We obtained 1.5 grams of a substance corresponding to 18 per cent. of the diiod-*m*-toluidine, crystallizing in small needles, melting at 185°–195°. Three more crystallizations gave a product melting constantly at 205°. This was difficultly soluble in all of the organic solvents and insoluble in dilute acids.

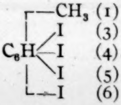
	Calculated for $C_7H_5NI_4$.	Found.
I	83.14	81.62

4,5,6-Triiod-m-*acettoluide*, $C_6HCH_3I_3NHCOCH_3$, from the base and acetyl chloride (acetic anhydride reacts slowly and incompletely), forms colorless needles which melt with effervescence at 265°. It is moderately soluble in alcohol and very difficultly soluble in hot water.

	Calculated for $C_9H_8ONI_3$.	Found.
N	2.66	2.77

2,3,4-Triiodtoluene,  $C_6H_2<\begin{matrix}CH_3 & (1)\\ I & (2)\\ I & (3)\\ I & (4)\end{matrix}$.—Ten grams of concentrated sulphuric acid were added to 100 cc. of absolute alcohol and three grams of 4,5,6-triiod-*m*-toluidine were dissolved in the warm mixture. We then slowly added three grams of sodium nitrite, waiting each time until the effervescence ceased. After all the nitrite was added the solution was heated for 1 hour on the steam bath and then poured into water. An oily substance separated which, on standing, solidified to a sticky mass. This was boiled in alcoholic solution with animal charcoal, filtered and, on cooling, 1.8 grams, or 62 per cent. of the calculated, of light brown crystals separated. On crystallizing twice more from alcohol radiating bunches of needles were obtained; they then melted constantly at 92°. This triiodtoluene is readily soluble in benzene and moderately soluble in alcohol. When mixed with 2,3,6-triiodtoluene, melting at 80°.5, the mixture melted at 60°–63°. The fact that the compounds are not identical shows that 5,6-diiod-*m*-toluidine iodates in the 4-position and proves the structure of 4,5,6-triiod-*m*-toluidine.

	Calculated for $C_7H_5I_3$.	Found.
I	81.06	79.16

3,4,5,6-Tetraiodtoluene,  $C_6H\begin{matrix}CH_3 & (1)\\ I & (3)\\ I & (4)\\ I & (5)\\ I & (6)\end{matrix}$.—Three and a half grams of 4,5,6-triiod-*m*-toluidine were diazotized and the diazo solution filtered from more or less undissolved material into a solution of potassium iodide. The product, after the usual treatment, weighed 2.7 grams, or 63 per cent. of the calculated. This, on crystallizing from benzene, melted to an oil at 284°–285°. It is moderately soluble in benzene and difficultly soluble in alcohol. From the former solvent it separates in straw-yellow needles.

	Calculated for $C_7H_4I_4$.	Found.
I	85.23	85.63

Pentaiodtoluene, $C_6I_5CH_3$.—Three and three-tenths grams of the tetraiod-*m*-toluidine were diazotized as in the previous experiments. Considerable (unaltered?) matter remained undissolved and the diazo solution was filtered into that of the potassium iodide. The diazo iodide formed in the filtrate was decomposed by heating and a solid substance separated which was dark but became almost colorless upon adding acid sodium sulphite. The yield was 0.8 gram, or 20 per cent. of the calculated. On recrystallizing this from benzene we obtained small needles having a dull yellow color and melting with decomposition at about 340°. This compound is difficultly soluble in the ordinary solvents.

	Calculated for $C_7H_3I_5$.	Found.
I	87.95	87.27

New Haven, Conn.,
October, 1910.

NOTE ON AMINOMETHYLBENZOIC ACIDS.

By Henry L. Wheeler and Charles Hoffman.

Since the appearance of our article on "Alkylation of Aromatic Amino Acids: Aminomethylbenzoic Acids" (third paper),[1] Professor Gabriel has had the kindness to call our attention to the work of his students on the nitration of *m*-toluic acid, which we regret to state had been overlooked by us.

Findeklee[2] and Müller[3] have shown that the nitro acid formed in chief amount (melting at 219°–220°) is 2-nitro-3-methylbenzoic acid (*2-Nitro-*m*-toluylsäure*) as originally stated by Jacobsen,[4] and not the isomer 2-nitro-5-methylbenzoic acid (*4-Nitrotoluylsäure*). The latter structure was assigned to this acid by Panaotovic[5] owing to the similarity in melting points of the corresponding amino acids. The acid is also represented in Beilstein's "Handbuch"[1] as having the 2,5-structure (*4-Nitrotoluylsäure*), which we accepted as correct.

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[1] This Journal, **44**, 113 (1910).

[2] Ber. d. chem. Ges., **38**, 3553 (1905).

[3] *Ibid.*, **42**, 430 (1909).

[4] *Ibid.*, **14**, 2353.

[5] J. prakt. Chem., [2] **33**, 62.

Some recent results obtained by us in the study of the structure of this compound will be communicated later. They show that the acid in question is, as Findeklee and Müller state, the 2-nitro-3-methylbenzoic acid and that the 2,5-structure is excluded.

Our supposed 2-amino-3-iod-5-methyl benzoic acid should therefore be viewed as 2-amino-3-methyl-5-iodbenzoic acid, the supposed 2-amino-5-methylbenzoic acid and its derivatives being 2-amino-3-methyl compounds.

NEW HAVEN, CONN.,
October, 1910.

THE CONDUCTIVITY, DISSOCIATION AND TEMPERATURE COEFFICIENTS OF CONDUCTIVITY AT 35°, 50° AND 65° OF AQUEOUS SOLUTIONS OF A NUMBER OF SALTS.

BY A. P. WEST AND HARRY C. JONES.[2]

[FOURTEENTH COMMUNICATION.]

This investigation is the direct continuation of the work of Clover and Jones[3] on the conductivities of a number of inorganic and organic compounds over the above-mentioned range in temperature, and also at a slightly higher temperature.

It is also part of a series of investigations which has been in progress in this laboratory for ten years, and on which thirteen papers[4] have already been published. Of these the papers of Douglas, West, Jacobson, Clover and White deal solely with the problem in question, while the other communications contain data that bear directly upon it.

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[1] III, 1337.

[2] This investigation was carried out with the aid of a grant from the Bache Fund.

[3] THIS JOURNAL, **43**, 187 (1910).

[4] Jones and Douglas: THIS JOURNAL, **26**, 428 (1901). Jones and Getman: *Ibid.*, **27**, 433 (1902). Jones and Getman: Z. physik. Chem., **46**, 244 (1903); Physic. Rev., **18**, 146 (1904). Jones and Getman: THIS JOURNAL, **31**, 303 (1904). Jones and Bassett: *Ibid.*, **33**, 534 (1905). Jones and Bassett: *Ibid.*, **34**, 290 (1905). Jones and West: *Ibid.*, **34**, 357 (1905). Jones: *Ibid.*, **35**, 445 (1906). Jones and Pearce: *Ibid.*, **38**, 683 (1907). Jones and Jacobson: *Ibid.*, **40**, 355 (1908). White and Jones: *Ibid.*, **42**, 520 (1909). Clover and Jones: *Ibid.*, **43**, 187 (1910). White and Jones: *Ibid.*, **44**, 159 (1910).

The problem is to determine the conductivity and dissociation of all of the more common electrolytes, inorganic and organic, at the ordinary temperatures at which chemical reactions take place. The work has been limited thus far to temperatures between 0° and 65°. We intend, however, to work at temperatures lower than 0°. Apparently we cannot work very much above 65° on account of the solubility of glass in water at high temperatures, but we may be able to overcome this difficulty.

Such data as we are now obtaining seem especially valuable, since it is over these ranges in temperature that most chemical reactions take place. We know that chemical reactions, in general, are ionic, and one of the first steps toward the understanding of the real meaning of reactions is to know the dissociation of the substances that take part in the reactions.

If we examine the literature we shall find that a fairly large number of conductivity measurements have been recorded. These, however, have been made chiefly at the temperatures 0°, 18°, and 25°, over a comparatively limited dilution, and embrace only a small part of the compounds with which the chemist has most frequently to deal. Indeed, our experience in searching for data in connection with the conductivity and dissociation of compounds at a given dilution and temperature is that in a large majority of cases the data that are desired are lacking. This applies especially to temperatures above 25° for which very few reliable data are available.

Further, the method of determining the conductivity of electrolytes, like scientific methods in general, is improved as time goes on. We have now better induction coils, better Wheatstone bridges, better conductivity cells, and far better rheostats than in the early days of the method. We are thus enabled to obtain more accurate data than formerly for all substances and at all temperatures.

In undertaking this elaborate investigation of the conductivity and dissociation of electrolytes in general, our first thought has been to secure the best possible apparatus and conditions. The coil used was the most improved form devised by Leeds and Northrup after experimenting a number of years on this problem. The cells were all of the ground-glass stoppered type, which has been used in this laboratory for some years. These cells are made of hard glass and soaked in water and acid a long time before using to diminish the solubility of the glass. The electrodes are tightly sealed into both tops and bottoms of the ground-glass stoppers to prevent the distance between the electrode plates from changing after the cell constants have been determined.

The rheostat used was made by Leeds and Northrup and calibrated both by them and by the Bureau of Standards in Washington.

At the beginning of the work the method and details of manipulation were essentially those used by Clover and Jones,[1] but as the investigation progressed a number of improvements were introduced.

Preparation of Solutions.

Since we worked over a range of temperature of only 30°, we found it convenient to prepare the solutions at the intermediate temperature, 50°, and then to use the solutions at the three temperatures, 35°, 50° and 65°. But since the volume of a solution varies with the temperature it was, of course, necessary to apply a correction at 35° and 65° to the volume of solutions made up at 50°.

When a standard solution is cooled from 50° to 35° there is a contraction in volume and a consequent increase in the concentration of the solution. The value of μ_v for any solution would, therefore, be slightly too large. The value of μ_v as found must be multiplied by the factor 0.994 for results at 35° when the solutions were made up at 50°. The correction factor for solutions made up at 50° and used at 65° is 1.0076.

The coefficient of expansion for distilled water is somewhat less than that for an aqueous solution. However, the difference in the coefficients for water and for our most concentrated solution is so small that it is negligible.

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[1] *Loc. cit.*

By making use of the above correction it was necessary to prepare only one set of solutions for each salt; and, consequently, much pure material and time were saved.

Solubility of Glass.

The solubility of glass at low temperatures is small, as is well known, but increases rapidly with the temperature and at high temperatures becomes very considerable. At 65° this factor must be taken into account in making conductivity measurements of aqueous solutions in glass vessels.

We reduced this effect to a minimum, and, as we convinced ourselves, to a negligible minimum, in the following way: All of the cells used in this work, as well as all of the bottles for preserving the solutions, were filled with a dilute solution of sodium hydroxide and heated for a number of hours. The glass apparatus was then thoroughly washed out with water. It was next filled with a dilute solution of hydrochloric acid and heated for a long time. The vessels were then carefully washed, filled with distilled water, and heated again. The above process was repeated a number of times.

In this way practically all of the more soluble material on the inner surface of the glass vessels was removed.

We convinced ourselves of this fact by allowing some of our most dilute solutions to stand for a long time, at elevated temperatures, in glass vessels thus treated, and determining the conductivity from time to time. From the slight change in the conductivity we showed that the question of the solubility of the glass was a negligible factor in this work.

Of course, all of the glass vessels used in this work were made of as nonsoluble glass as possible.

Cell Constants.

Clover and Jones experienced some difficulty in securing reliable cell constants. Results obtained by them seemed to indicate that the cell constants did not remain exactly constant when the cells were used at different temperatures. When the cells were heated the glass and electrodes expanded and this would produce some change in the constants.

We calculated the magnitude of this change from the longitudinal and cubical expansion of glass, and found that for the conditions under which we worked it was negligible.

The work of Clover and Jones, however, showed that when the cells are heated the change which they undergo persists for a considerable time. The conductivity of a solution was determined at 35°. The solution was then heated to 65° in the conductivity cell and allowed to remain at that temperature in the cell for about one hour. It was then cooled to 35° and the conductivity redetermined after temperature equilibrium had been re-established at this temperature.

In a number of cases the second determination of conductivity at 35° differed slightly from the first, showing that the cell constants had undergone a slight change during heating, as we had convinced ourselves that the slight change in conductivity under these conditions was not due to dissolved glass. In all of these cases, however, when the solution, after heating, was allowed to remain in the cell at 35° for about three hours, the second conductivity determination always agreed with the first.

This showed that whatever change the cell underwent at the higher temperature disappeared in time when the cell was kept at the lower temperature.

Based upon this fact, we devised and used the following method for determining the cell constants and for making the conductivity measurements, the object being to make the measurements under as nearly as possible the same conditions as were employed in determining the cell constants.

The standard solution of potassium chloride, either 0.02 N or 0.002 N, depending upon the distance apart of the electrode plates, was placed in the conductivity cell. The cell was then heated to 50°, and after remaining at that temperature for about an hour was cooled to 20°. *As soon as temperature equilibrium* was established at 20° the conductivity readings were made and the cell constants calculated.

The same method was employed in determining the conductivity of solutions. The solutions in the cells were first heated to 50° and allowed to remain at that temperature for about an hour. The cells were then placed in a bath and cooled down to 35°, and as soon as temperature equilibrium was established the conductivity readings were made. The cells were then placed in the 50° bath and after the solutions had come to this temperature the conductivity determinations were made. They were then transferred to the 65° bath and the corresponding conductivities determined.

We regard this method of determining cell constants and of carrying out conductivity measurements as important. If the cell constant is determined at 20° and conductivity measurements made in it at higher temperatures, the calculated constant is not the true constant for the cell. If, on the other hand, the cell is first heated to 50°, cooled to 20°, and the constant then quickly determined at this temperature we have comparable conditions for determining the constant of the cell and the conductivity of the solutions. The mean of 35° and 65° is 50° and it requires about three hours for the cell to acquire its normal condition at 20°. By this method we determine the cell constant after the cell has undergone its temporary small change at the higher temperature.

Experiments similar to those carried out by Clover and Jones, *i. e.*, determining the conductivity of a solution at 35°, heating it and then cooling it to 35° again and redetermining its conductivity, were carried out. We found practically no change in the conductivity of a solution before and after heating, provided the cell constants had been determined as described above.

Another good reason for warming the solutions in the cells before determining the cell constants and the conductivities of the solutions is to avoid the presence of air bubbles on the electrode plates. By first heating the solutions in the cells to 50° and then removing the air bubbles gathered on the plates, no further disturbance due to this change is encountered in determining the conductivities of these solutions at lower temperatures.

The cells when not in use were filled with redistilled water and kept continually in a bath at a temperature of from 45° to 50°. All of the cell constants were redetermined once in about every two weeks. Only very slight changes were found in any of the constants during this entire work.

Ammonium Bromide.

The pure salt was heated for several hours in an air bath at 130°. The standardization of the original solution was effected by weighing out the amount of salt necessary to make a 0.25 N solution:

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	139.4	81.29	174.2	78.8	210.6	78.7
8	145.0	84.55	182.2	82.4	220.9	82.5
32	156.2	91.08	196.3	88.8	239.3	89.4
128	163.2	95.16	206.2	93.3	250.9	93.7
512	168.5	98.25	213.7	96.7	259.8	97.0
1024	171.5	100.0	221.0	100.0	267.6	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.32	1.66	2.43	1.39
8	2.48	1.72	2.58	1.42
32	2.67	1.71	2.87	1.46
128	2.87	1.76	2.98	1.45
512	3.01	1.78	3.08	1.44
1024	3.30	1.92	3.11	1.41

Ammonium Bisulphate.

The strength of the original solution was obtained by determining the sulphur as barium sulphate.

Conductivity.

V.	μ_v 35°.	μ_v50°.	μ_v65°.
4	248.6	268.0	282.1
16	308.2	334.4	351.3
32	349.7	381.3	403.2
128	435.0	482.3	526.9
512	523.2	603.7	669.4
2048	556.2	656.5	752.7

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.29	0.52	0.94	0.35
16	1.75	0.57	1.13	0.34
32	2.11	0.60	1.46	0.38
128	3.15	0.72	2.97	0.62
512	5.36	1.02	4.38	0.72
2048	6.68	1.20	6.41	0.97

Sodium Iodide.

The original solution was made up by direct weighing. The salt was heated for several days at 150° to constant weight.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	115.9	80.00	146.2	78.2	179.0	76.5
8	121.0	83.5	152.6	81.6	187.5	80.1
32	128.6	88.7	163.4	87.4	200.2	85.5
128	136.2	94.0	173.2	92.6	213.2	91.1
512	142.7	98.5	180.6	96.6	222.0	94.8
1024	144.9	100.0	187.0	100.0	234.1	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond units.	Per cent.	Cond. units.	Per cent.
4	2.02	1.74	2.19	1.49
8	2.11	1.74	2.33	1.52
32	2.32	1.80	2.46	1.50
128	2.47	1.81	2.67	1.54
512	2.53	1.77	2.76	1.53
1024	2.81	1.94	3.14	1.67

Sodium Carbonate.

The anhydrous salt was heated for several hours at 130°. The original solution was made up by weighing. As in the case of potassium carbonate, the dissociation was not calculated. The salt is, of course, considerably hydrolyzed, especially at the higher temperatures.

Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
4	145.9	190.9	237.9
8	168.5	219.6	271.9
32	209.0	272.1	343.4
128	241.9	318.3	403.3
512	258.0	336.7	424.7
1024	269.7	350.1	439.5

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	3.00	2.05	3.13	1.64
8	3.41	2.02	3.49	1.59
32	4.21	2.0	4.74	1.74
128	5.09	2.10	5.67	1.78
512	5.25	2.04	5.87	1.74
1024	5.36	1.99	5.96	1.70

Sodium Acetate.

The original solution was made up by direct weighing. The sample of salt used was dried in an air bath for several days at 120°.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	75.14	75.5	97.28	74.6	121.0	73.5
8	81.66	82.1	106.0	81.3	131.7	80.1
32	91.10	91.5	117.9	90.4	147.7	89.8
128	97.13	97.6	125.7	96.4	157.5	95.7
512	99.40	99.9	129.3	99.2	162.7	98.9
2048	99.50	100.0	130.4	100.0	164.5	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.47	1.95	1.58	1.62
8	1.62	1.98	1.71	1.61
32	1.79	1.96	1.99	1.69
128	1.90	1.95	2.12	1.69
512	1.99	2.00	2.23	1.72
2048	2.06	2.07	2.27	1.74

Potassium Iodide.

The sample of salt used was heated in an air bath for several days at a temperature of 120°. The 0.25 N solution was made up by direct weighing.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	*a.*	μ_v.	*a.*	μ_v.	*a.*
4	139.9	83.5	174.8	80.3	212.7	79.3
8	144.8	86.5	181.5	83.4	221.2	82.5
32	154.0	91.9	194.2	89.2	235.8	87.9
128	160.9	96.1	202.0	92.8	248.0	92.5
512	166.2	99.2	213.3	98.0	261.4	97.5
1024	167.5	100.0	217.6	100.0	268.1	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.33	1.66	2.53	1.45
8	2.45	1.69	2.65	1.46
32	2.68	1.74	2.77	1.43
128	2.74	1.70	3.07	1.52
512	3.14	1.89	3.22	1.51
1024	3.34	1.99	3.37	1.55

Potassium Bisulphate.

The sample of salt used was heated in an air bath for several days at 130°.

Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
4	246.7	265.8	278.9
8	276.0	298.8	313.3
32	353.8	388.4	408.9
128	451.7	502.9	536.7
512	537.4	616.0	675.6
2048	579.7	675.0	747.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.27	0.51	0.87	0.33
8	1.52	0.55	0.97	0.32
32	2.31	0.65	1.37	0.35
128	3.41	0.75	2.25	0.45
512	5.24	1.22	3.97	0.64
2048	6.35	1.10	4.80	0.71

Potassium Carbonate.

The pure anhydrous salt was dried for some hours at 130° and the mother solution made up by weighing.

Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
4	187.9	237.0	288.0
8	199.8	252.1	308.6
32	233.2	297.5	369.9
128	261.7	334.9	422.8
512	278.5	361.0	451.2
1024	285.5	373.3	467.3

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	3.27	1.74	3.40	1.43
8	3.49	1.75	3.77	1.49
32	4.29	1.79	4.83	1.62
128	4.88	1.86	5.86	1.75
512	5.50	1.97	6.01	1.66
1024	5.85	2.05	6.27	1.69

Potassium Dichromate.

The sample of salt used was heated for some hours to constant weight. The 0.25 N solution was made up by direct weighing. The true value of μ_∞ is probably reached at a dilution greater than 2048 liters, so our values for α are, perhaps, only approximations.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	218.0	76.4	272.1	74.3	326.9	72.8
8	233.7	81.9	292.4	79.8	352.9	78.6
32	261.9	91.7	327.3	89.3	396.9	88.4
128	276.3	96.8	346.0	94.4	417.9	93.1
512	279.2	97.8	351.7	96.0	426.8	95.1
2048	285.5	100.0	366.4	100.0	448.9	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	3.61	1.65	3.65	1.34
8	3.91	1.67	4.03	1.37
32	4.36	1.66	4.64	1.42
128	4.65	1.68	4.79	1.38
512	4.83	1.73	5.01	1.42
2048	5.39	1.88	5.50	1.50

Potassium Ferrocyanide.

The original solution was made up by direct weighing.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	334.5	44.5	414.5	44.0	495.6	43.0
8	361.7	48.1	450.6	47.8	543.0	47.1
32	425.6	56.6	535.0	56.8	651.0	56.4
128	521.6	69.3	663.1	70.4	808.3	70.1
512	637.1	84.7	818.7	86.9	1006.3	87.2
2048	723.6	96.2	915.4	97.2	1121.3	97.2
8192	752.4	100.0	941.9	100.0	1153.2	190.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	5.33	1.59	5.41	1.30
8	5.93	1.64	6.16	1.36
32	7.29	1.71	7.73	1.44
128	9.43	1.81	9.68	1.46
512	12.11	1.90	12.51	1.53
2048	12.79	1.77	13.73	1.50
8192	12.63	1.68	14.08	1.50

Lithium Bromide.

The standardization of the original solution was effected by direct weighing. The salt was heated in an air bath for several days at 130°.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	108.0	80.5	137.0	79.0	168.4	77.9
8	109.6	81.7	139.3	80.4	170.4	78.8
32	118.3	88.2	150.7	87.0	186.4	86.3
128	125.5	93.6	160.0	92.3	198.0	91.6
512	132.0	98.4	169.7	97.9	213.6	98.8
2048	134.1	100.0	173.3	100.0	216.1	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.93	1.78	2.09	1.52
8	1.98	1.81	2.07	1.49
32	2.16	1.83	2.38	1.58
128	2.30	1.83	2.53	1.58
512	2.51	1.90	2.93	1.72
2048	2.61	1.94	2.85	1.64

Lithium Nitrate.

The salt was heated for several days at 120° to constant weight. The mother solution was made up by direct weighing.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	95.04	76.9	119.6	74.6	146.4	74.0
8	101.7	82.3	128.6	80.2	157.7	79.7
32	108.0	87.4	138.2	86.2	170.1	86.0
128	116.8	94.5	150.1	93.6	184.9	93.5
512	119.7	96.8	154.2	96.2	192.4	97.3
1024	123.6	100.0	160.3	100.0	197.8	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.63	1.71	1.78	1.48
8	1.79	1.76	1.94	1.51
32	2.01	1.86	2.13	1.54
128	2.22	1.90	2.32	1.53
512	2.30	1.92	2.55	1.65
1024	2.45	1.98	2.50	1.56

Lithium Sulphate.

The sample of salt used was dried for several days at 150°. The original solution was made up by direct weighing.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	132.8	51.5	168.8	49.8	207.8	48.2
8	154.9	60.0	197.3	58.2	242.7	56.3
32	190.9	74.0	245.7	72.5	301.8	70.0
128	225.2	87.3	290.5	85.7	362.3	84.1
512	247.7	96.0	324.3	95.7	405.0	94.0
1024	256.8	99.5	336.3	99.3	425.5	98.7
2048	258.0	100.0	338.7	100.0	430.8	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.40	1.80	2.60	1.54
8	2.83	1.82	3.00	1.52
32	3.65	1.91	3.74	1.52
128	4.35	1.93	4.78	1.64
512	5.10	2.06	5.38	1.66
1024	5.30	2.06	5.95	1.77
2048	5.38	2.09	6.14	1.81

Calcium Bromide.

The exact strength of the original solution was determined by titrating the bromine with a standard solution of silver nitrate.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
8	204.5	67.5	264.2	67.9	328.7	68.1
32	250.0	82.5	316.7	81.5	387.8	80.4
128	273.4	90.2	346.4	89.1	426.5	88.4
512	292.6	96.6	372.4	95.8	461.5	95.7
2048	303.0	100.0	388.6	100.0	482.4	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	3.98	1.94	4.30	1.63
32	4.45	1.78	4.74	1.50
128	4.86	1.78	5.34	1.54
512	5.32	1.82	5.94	1.59
2048	5.71	1.88	6.25	1.61

Calcium Nitrate.

The strength of the original solution was obtained by direct weighing. The salt was dried in an air bath for several days at 130° to constant weight.

Conductivity and Dissociation.

	35°.		50°		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	168.2	58.0	212.6	57.2	258.1	56.3
8	187.0	64.5	237.9	64.0	287.8	62.8
32	223.0	76.9	285.6	76.8	350.6	76.5
128	253.3	87.4	323.1	86.9	397.7	86.8
512	276.3	95.3	349.4	94.0	432.5	94.4
2048	289.9	100.0	371.8	100.0	458.3	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.96	1.76	3.03	1.42
8	3.39	1.81	3.33	1.39
32	4.17	1.87	4.33	1.51
128	4.64	1.83	4.97	1.53
512	4.87	1.77	5.54	1.58
2048	5.46	1.89	5.77	1.55

Calcium Formate.

The strength of the original solution was obtained by determining the calcium as the sulphate.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	128.5	58.1	161.3	56.3	195.2	54.5
8	150.9	68.2	190.0	66.3	230.8	64.4
32	185.9	84.0	235.5	82.2	287.8	80.3
128	210.2	95.0	268.6	93.7	331.5	92.5
512	220.7	99.7	283.2	98.8	349.6	97.6
2048	221.3	100.0	286.6	100.0	358.2	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.19	1.70	2.26	1.40
8	2.61	1.73	2.72	1.43
32	3.31	1.78	3.49	1.48
128	3.89	1.85	4.13	1.54
512	4.17	1.89	4.43	1.56
2048	4.35	1.96	4.77	1.66

Strontium Bromide.

The strength of the mother solution was determined by Mohr's method.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	203.2	64.1	256.3	63.1	312.7	62.4
8	222.8	70.3	282.5	69.6	343.7	68.6
32	250.1	78.9	316.9	78.1	388.7	77.6
128	278.9	87.9	356.2	87.7	437.6	87.3
512	299.1	94.3	380.3	93.7	470.1	93.8
2048	317.1	100.0	405.9	100.0	501.0	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	3.54	1.74	3.76	1.46
8	3.98	1.78	4.08	1.44
32	4.45	1.78	4.79	1.51
128	5.15	1.84	5.43	1.52
512	5.41	1.81	5.99	1.57
2048	5.92	1.86	6.34	1.56

Strontium Nitrate.

The original solution was made up by direct weighing; the salt was heated for several days at 120°.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	162.4	56.1	206.1	55.8	253.7	55.0
8	185.2	63.9	234.3	63.4	288.0	62.5
32	223.9	77.3	284.2	76.9	354.4	76.9
128	253.0	87.4	322.5	87.3	400.7	86.9
512	276.6	95.5	351.7	92.2	441.0	95.7
2048	289.6	100.0	369.3	100.0	460.9	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.91	1.79	3.17	1.54
8	3.27	1.77	3.58	1.53
32	4.02	1.80	4.68	1.65
128	4.63	1.83	5.21	1.62
512	5.01	1.81	5.95	1.69
2048	5.31	1.83	6.11	1.65

Strontium Acetate.

The concentration of the mother solution was obtained by determining the strontium as sulphate.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	104.6	48.4	132.4	47.3	160.9	45.4
8	120.9	56.0	153.7	54.9	193.8	54.7
32	162.6	75.3	207.7	74.2	256.5	72.4
128	190.1	88.0	244.3	87.3	305.0	86.1
512	208.2	96.4	267.0	95.4	336.6	95.0
2048	215.9	100.0	279.9	100.0	354.2	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.85	1.77	1.90	1.43
8	2.19	1.81	2.67	1.73
32	3.01	1.85	3.25	1.56
128	3.61	1.90	4.05	1.66
512	3.92	1.88	4.64	1.74
2048	4.27	1.98	4.95	1.77

Barium Nitrate.

The specimen of salt used was dried for several days at 130° and then kept in a desiccator until used. The concentration of the mother solution was obtained by weighing.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	150.8	50.9	192.6	51.3	236.5	50.9
8	177.9	60.1	225.3	60.0	274.7	59.2
32	221.9	74.9	281.5	74.9	345.1	74.4
128	256.8	86.7	326.4	86.9	401.8	86.6
512	282.3	95.3	358.6	95.5	443.1	95.4
2048	296.2	100.0	375.5	100.0	464.1	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.78	1.84	2.93	1.52
8	3.16	1.78	3.29	1.46
32	3.97	1.79	4.24	1.51
128	4.64	1.81	5.03	1.54
512	5.08	1.80	5.63	1.57
2048	5.28	1.78	5.91	1.57

Barium Formate.

The concentration of the original solution was obtained by determining the barium as sulphate.

Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
4	138.6	174.0	209.5
8	157.7	193.7	232.8
32	203.3	257.6	314.9
128	223.1	283.2	344.5
512	235.5	299.1	367.9

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.36	1.70	2.37	1.36
8	2.40	1.52	2.61	1.34
32	3.62	1.78	3.82	1.48
128	4.01	1.80	4.09	1.44
512	4.17	1.77	4.59	1.53

Barium Acetate.

The exact strength of the original solution was ascertained by determining the barium as sulphate.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	114.7	51.6	142.8	49.9	172.2	48.2
8	125.5	56.5	156.6	53.5	188.8	52.8
32	173.3	78.0	221.8	77.5	273.5	76.6
128	194.4	87.5	250.7	87.6	311.5	87.2
512	214.7	96.7	276.7	96.7	345.0	96.6
2048	222.1	100.0	286.2	100.0	357.2	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.87	1.63	1.96	1.37
8	2.07	1.65	2.15	1.37
32	3.23	1.86	3.43	1.55
128	3.75	1.93	4.05	1.61
512	4.13	1.92	4.55	1.64
2048	4.27	1.92	4.73	1.65

Magnesium Bromide.

The strength of the original solution was determined by titrating a diluted portion of it with a 0.1 N silver nitrate solution. A portion of the original solution was then made exactly 0.25 N and checked by another titration.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	199.1	67.7	251.2	66.6	308.3	65.4
8	208.3	70.8	263.2	69.8	324.4	68.8
32	234.1	79.6	297.6	78.9	367.7	78.0
128	261.1	88.7	332.4	88.2	412.8	87.6
512	279.0	94.8	358.0	95.0	445.5	94.5
2048	294.2	100.0	377.0	100.0	471.3	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	3.47	1.74	3.81	1.52
8	3.66	1.75	4.08	1.55
32	4.23	1.81	4.67	1.57
128	4.75	1.82	5.36	1.61
512	5.27	1.89	5.83	1.63
2048	5.52	1.88	6.25	1.66

Magnesium Formate.

The strength of the original solution was obtained by determining the magnesium as the pyrophosphate.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	107.4	48.7	135.7	47.7	164.4	46.7
8	130.6	59.3	165.2	58.1	201.4	57.2
32	166.7	75.7	212.8	74.9	261.8	74.4
128	196.8	89.3	253.8	89.3	313.8	89.1
512	212.0	92.6	273.7	96.3	337.9	96.0
2048	220.3	100.0	284.2	100.0	352.0	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.89	1.76	1.91	1.41
8	2.31	1.77	2.41	1.46
32	3.07	1.84	3.27	1.54
128	3.80	1.93	4.00	1.57
512	4.11	1.94	4.28	1.56
2048	4.26	1.93	4.52	1.59

Magnesium Acetate.

The strength of the mother solution was obtained by determining the magnesium as the pyrophosphate.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	87.0	43.7	110.8	42.9	136.1	41.6
8	109.0	54.8	138.8	53.8	171.2	52.3
32	145.2	73.0	187.1	72.4	231.7	70.8
128	171.4	86.2	219.7	85.1	276.6	84.5
512	188.8	94.9	245.9	95.2	310.9	95.0
2048	198.9	100.0	258.2	100.0	327.2	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.59	1.83	1.69	1.52
8	1.99	1.83	2.16	1.56
32	2.79	1.92	2.97	1.59
128	3.22	1.88	3.79	1.72
512	3.81	2.01	4.33	1.76
2048	3.95	1.99	4.60	1.78

Cadmium Chloride.

The exact strength of the original solution was obtained by titrating the chlorine with a 0.1 N solution of silver nitrate.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	72.74	26.2	89.9	25.3	106.5	24.2
8	94.54	34.0	117.3	33.0	139.6	31.7
32	143.6	51.7	179.9	50.6	216.2	49.1
128	196.0	70.5	247.1	69.5	300.0	68.1
512	243.6	87.6	309.5	87.1	378.8	86.0
2048	278.0	100.0	355.4	100.0	440.5	100.0

Temperature Coefficients.

	35°–65°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.14	1.57	1.12	1.25
8	1.52	1.61	1.49	1.27
32	2.42	1.68	2.42	1.34
128	3.41	1.74	3.52	1.42
512	4.39	1.80	4.62	1.49
2048	5.16	1.86	5.67	1.59

Cadmium Bromide.

The purified salt was dissolved in conductivity water and the strength of the solution ascertained by determining the bromine as silver bromide.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	*α.*	μ_v.	*α.*	μ_v.	*α.*
4	64.25	23.5	80.3	22.9	96.4	22.1
8	85.25	31.2	107.0	30.5	128.5	29.5
32	132.4	48.4	167.6	47.8	202.3	46.4
128	183.7	67.1	234.0	66.7	286.4	65.7
512	234.6	85.7	299.1	85.3	369.1	84.6
2048	273.6	100.0	350.7	100.0	436.0	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.07	1.66	1.07	1.33
8	1.45	1.70	1.43	1.34
32	2.35	1.77	2.31	1.38
128	3.35	1.82	3.49	1.49
512	4.30	1.83	4.67	1.56
2048	5.14	1.88	5.69	1.62

Cadmium Iodide.

The salt was dried in a desiccator over calcium chloride for a week or more. The original solution was made by direct weighing.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	*α.*	μ_v.	*α.*	μ_v.	*α.*
4	48.45	18.7	61.70	18.5	74.96	18.1
8	59.94	23.2	77.16	23.1	94.61	22.8
32	100.2	38.8	130.4	39.1	161.3	38.9
128	157.7	61.0	204.8	61.4	254.8	61.4
512	213.3	82.5	276.7	83.0	345.5	83.3
2048	258.5	100.0	333.4	100.0	414.5	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	0.88	1.82	0.88	1.42
8	1.15	1.92	1.16	1.50
32	2.01	2.00	2.06	1.58
128	3.14	1.99	3.33	1.62
512	4.23	1.98	4.59	1.66
2048	4.99	1.93	5.41	1.62

Zinc Sulphate.

The mother solution was made up by weighing.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	84.78	28.5	104.6	27.1	122.2	25.6
8	95.66	32.1	117.8	30.6	137.2	28.7
32	128.8	43.3	159.3	41.3	186.9	39.1
128	174.0	58.4	217.9	56.5	259.6	54.4
512	225.1	77.4	286.5	74.3	347.3	72.7
2048	263.8	88.6	338.4	87.8	417.3	87.4
8192	297.8	100.0	385.5	100.0	477.4	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.32	1.56	1.17	1.12
8	1.47	1.54	1.29	1.10
32	2.03	1.58	1.84	1.15
128	2.93	1.68	2.78	1.27
512	4.09	1.82	4.05	1.41
2048	4.97	1.88	5.26	1.55
8192	5.85	1.96	6.13	1.59

Manganese Chloride.

The strength of the original solution was obtained by determining the chlorine gravimetrically. By proper dilution a quarter-normal solution was prepared and the other solutions were made from this.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	173.8	59.8	218.0	58.2	263.5	56.6
8	194.1	66.8	245.3	65.5	297.9	63.9
32	226.9	78.1	288.5	77.1	355.0	76.2
128	257.0	88.4	329.0	87.9	406.8	87.3
512	277.9	95.6	357.6	95.5	444.7	95.5
2048	290.7	100.0	374.3	100.0	465.8	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.95	1.69	3.03	1.39
8	3.41	1.75	3.51	1.43
32	4.11	1.81	4.43	1.53
128	4.80	1.87	5.19	1.58
512	5.31	1.91	5.81	1.62
2048	5.57	1.92	6.10	1.63

Cobalt Chloride.

The strength of the original solution was ascertained by means of several gravimetric determinations of the chlorine. A portion of the original solution was then made exactly 0.25 N and the other solutions prepared from this by dilution. It is apparent from the tables that the salt is somewhat hydrolyzed in very dilute solutions.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	188.3	66.1	226.4	61.4	274.3	59.2
8	197.6	69.3	249.4	67.6	302.5	65.3
32	227.7	79.9	288.7	78.3	355.6	76.8
128	255.1	89.5	326.7	88.6	404.2	87.3
512	275.5	96.6	352.2	95.5	442.8	95.6
2048	285.1	100.0	368.7	100.0	463.2	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.54	1.35	3.19	1.41
8	3.45	1.74	3.54	1.42
32	4.07	1.79	4.46	1.54
128	4.77	1.87	5.17	1.58
512	5.11	1.86	6.04	1.71
2048	5.57	1.95	6.30	1.71

Cobalt Bromide.

The exact strength of the original solution was obtained by determining the bromine as silver bromide. The other solutions were, of course, made by dilution. It is apparent from the tables that the results are of the same general nature as those obtained with the other cobalt salts we have studied.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	189.8	65.7	239.0	64.5	289.6	62.4
8	205.1	71.0	259.4	70.0	315.7	68.0
32	235.6	81.5	299.5	80.8	367.3	79.1
128	258.0	89.3	329.5	88.9	406.7	87.6
512	275.6	95.4	353.1	95.3	436.6	94.0
2048	289.0	100.0	370.6	100.0	464.3	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	3.28	1.73	3.37	1.41
8	3.60	1.75	3.75	1.44
32	4.26	1.81	4.52	1.51
128	4.77	1.85	5.15	1.56
512	5.17	1.87	5.57	1.58
2048	5.44	1.88	6.25	1.68

Cobalt Nitrate.

The strength of the original solution was obtained by determining the cobalt as cobalt sulphate. The other solutions were obtained by dilution. As in the case of cobalt chloride the salt is probably hydrolyzed in dilute solutions.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	172.8	62.2	216.8	61.0	263.5	60.0
8	190.7	68.7	239.7	67.5	291.4	66.4
32	218.5	78.7	276.9	77.9	340.2	77.5
128	244.0	87.9	310.1	87.3	384.0	87.5
512	262.9	94.7	334.7	94.2	414.6	94.4
2048	277.7	100.0	355.3	100.0	439.0	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.93	1.69	3.11	1.43
8	3.27	1.71	3.45	1.44
32	3.89	1.78	4.22	1.52
128	4.41	1.81	4.93	1.59
512	4.79	1.82	5.33	1.59
2048	5.17	1.86	5.58	1.57

Cobalt Acetate.

The exact strength of the original solution was ascertained by determining the cobalt as sulphate.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
4	73.2	91.4	110.9
8	86.9	106.8	131.2
32	139.1	175.8	217.1
128	162.0	206.9	256.4
512	187.4	241.9	300.7
2048	200.1	260.4	326.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.21	1.65	1.30	1.42
8	1.33	1.53	1.63	1.52
32	2.45	1.76	2.75	1.56
128	2.99	1.84	3.30	1.59
512	3.63	1.94	3.92	1.62
2048	4.02	2.01	4.37	1.68

Nickel Chloride.

The concentration of the mother solution was obtained by determining the chlorine, gravimetrically, as silver chloride.

Salts of nickel, like those of cobalt, are probably hydrolyzed to some extent at high dilutions.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
4	174.9	61.1	218.0	59.3	266.0	58.4
8	194.5	67.9	247.3	67.2	301.5	66.2
32	225.5	78.8	288.1	78.3	354.7	77.9
128	251.4	87.8	321.4	87.4	398.4	87.5
512	270.6	94.5	344.4	93.6	426.1	93.5
2048	286.2	100.0	367.9	100.0	455.5	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.87	1.64	3.20	1.46
8	3.52	1.81	3.61	1.46
32	4.17	1.85	4.44	1.54
128	4.66	1.85	5.13	1.59
512	4.92	1.82	5.45	1.58
2048	5.45	1.90	5.84	1.59

Aluminium Nitrate.

The strength of the mother solution was ascertained by several gravimetric determinations of the aluminium.

Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
32	204.2	260.5	323.0
128	233.2	301.2	381.1
512	265.9	350.8	458.4
2048	296.3	402.2	535.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	3.75	1.84	4.16	1.60
128	4.53	1.94	5.33	1.77
512	5.66	2.13	7.17	2.04
2048	7.06	2.38	8.85	2.20

Aluminium Sulphate.

After several crystallizations the purified salt was dissolved in conductivity water and the strength of the original solution determined by estimating the aluminium as the oxide.

Conductivity and Dissociation.

	35°.		50°.		65°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
8	137.2	24.5	167.6	23.1	188.4	20.3
32	197.1	35.2	234.5	32.3	264.6	28.5
128	274.1	49.0	333.3	46.0	387.6	41.7
512	388.1	69.4	483.8	66.7	581.6	62.6
2048	559.3	100.0	725.0	100.0	929.4	100.0

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	2.03	1.48	1.39	0.83
32	2.49	1.26	2.01	0.86
128	3.95	1.44	3.62	1.09
512	6.38	1.64	6.52	1.35
2048	11.05	1.98	13.63	1.88

Chromium Nitrate.

As in the case of chromium chloride, the strength of the mother solution was obtained by determining the chromium gravimetrically as chromic oxide. Results of the same general character were obtained with chromium nitrate as with the chloride.

Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
4	228.2	289.7	365.2
8	263.0	334.7	419.4
32	321.4	414.8	519.1
128	395.0	517.6	663.2
512	473.2	627.6	809.0
2048	554.3	732.6	937.4

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	4.10	1.80	5.03	1.73
8	4.78	1.82	5.65	1.69
32	6.23	1.94	6.95	1.68
128	8.17	2.07	9.71	1.87
512	10.23	2.18	12.09	1.93
2048	11.88	2.14	13.65	1.86

Chromium Acetate.

The concentration of the mother solution was obtained by determining the chromium as the oxide.

Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
4	39.0	49.5	58.5
8	44.5	53.6	65.5
32	55.5	71.1	89.0
128	62.4	81.0	111.3
512	74.4	97.5	135.1
2048	91.8	120.2	169.1

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	0.70	1.79	0.60	1.21
8	0.61	1.37	0.79	1.47
32	1.04	1.87	1.19	1.67
128	1.24	1.99	2.02	2.49
512	1.54	2.07	2.51	2.57
2048	1.89	2.06	3.26	2.71

Uranyl Chloride.

The strength of the original solution was determined in the same manner as in the case of uranyl nitrate, the uranium being weighed as the green oxide, U_3O_8. The salt is, no doubt, considerably hydrolyzed in dilute solution.

Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
4	220.4	274.6	333.2
8	253.5	318.9	387.8
32	301.4	380.3	473.2
128	342.0	439.4	548.5
512	379.4	491.1	610.6
2048	418.5	546.8	693.7

Temperature Coefficients.

	35°-50°.		50°-65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	3.61	1.64	3.91	1.42
8	4.36	1.72	4.59	1.44
32	5.26	1.74	6.19	1.63
128	6.49	1.90	7.27	1.65
512	7.45	1.96	7.97	1.62
2048	8.55	2.04	9.79	1.79

Uranyl Nitrate.

The strength of the original solution was determined by precipitating with ammonia and igniting the precipitate to the green uranoso-uranic oxide, U_3O_8.

Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
4	176.0	220.1	268.3
8	199.2	251.2	307.1
32	233.8	298.0	372.0
128	275.4	354.6	444.7
512	303.2	395.8	502.0
2048	349.0	460.8	585.3

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.94	1.67	3.21	1.46
8	3.46	1.74	3.73	1.48
32	4.28	1.83	4.93	1.65
128	5.28	1.92	6.01	1.69
512	6.17	2.03	7.08	1.79
2048	7.45	2.13	8.30	1.80

Uranyl Sulphate.

The strength of the original solution was ascertained by determining the uranium as the oxide U_3O_8. From the original solution the other solutions were prepared by dilution. As in the case of uranyl acetate, the temperature coefficients expressed in percentages decrease with increase in dilution.

Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
16	90.1	110.5	131.3
32	115.9	139.5	162.8
128	155.0	185.0	213.7
512	219.0	264.3	303.7

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
16	1.36	1.51	1.39	1.26
32	1.57	1.35	1.55	1.11
128	2.00	1.29	1.91	1.03
512	3.02	1.38	2.63	0.99

Uranyl Acetate.

The strength of the mother solution was obtained by determining the uranium. The temperature coefficients expressed in percentages decrease with increase in dilution. This is rather remarkable, the opposite effect being usually obtained.

Conductivity.

V.	μ_v 35°.	μ_v 50°.	μ_v 65°.
16	48.06	59.34	71.36
32	54.92	67.36	80.47
128	72.26	87.65	103.4
512	92.92	111.3	130.0
2048	118.4	141.4	165.4

Temperature Coefficients.

	35°–50°.		50°–65°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
16	0.75	1.56	0.80	1.34
32	0.83	1.51	0.87	1.29
128	1.02	1.41	1.05	1.19
512	1.22	1.31	1.25	1.12
2048	1.53	1.29	1.60	1.13

Discussion of Results.

That the work done in this laboratory is already of fairly wide scope can be seen from the following statement. The conductivities of the following inorganic compounds have been measured from 0° to 35°:

The bromide, iodide, nitrate, carbonate, diphosphate and acetate of sodium; the chloride, bromide, iodide, nitrate, acid sulphate, sulphate, carbonate, sulphocyanate, chromate, dichromate and ferrocyanide of potassium; the chloride, bromide, nitrate and sulphate of lithium; the chloride and bromide of ammonium; the chloride, bromide and nitrate of calcium; the chloride, bromide and nitrate of strontium; the chloride, bromide, nitrate, formate and acetate of barium; the chloride and sulphate of magnesium; zinc sulphate; the chloride, nitrate, sulphate and acetate of cobalt; the chloride, nitrate, sulphate and acetate of nickel; the chloride and nitrate of manganese; lead nitrate; the chloride and nitrate of iron; the chloride and nitrate of chromium; the chloride, bromide and nitrate of copper; and hydrochloric, nitric and sulphuric acids.

The conductivities of the following organic acids have been measured from 0° to 35°: Acetic, propionic, butyric, isobutyric, phenylacetic, mandelic, hippuric, malonic, succinic, maleic, fumaric, crotonic, citraconic, mesaconic, itaconic, racemic, pyrotartaric, citric, pyromucic, benzoic, *o*-toluic, *m*-toluic, *p*-toluic, *o*-phthalic, cinnamic, salicylic, *m*-hydroxybenzoic, *p*-hydroxybenzoic, gallic, *o*-aminobenzoic, *p*-aminobenzoic, metanilic, sulphanilic, oxanilic, benzilic, *p*-nitrobenzoic, *p*-toluenesulphonic, α-methylaminosulphonic (1,4), *m*-nitrobenzenesulphonic, nitrotoluenesulphonic (4,1,2), trichloracetic, picric, *o*-nitrobenzoic, *m*-nitrobenzoic and oxalic.

The conductivities of the following compounds, including those recorded in this paper, have been measured from 35° to 65°:

The bromide, iodide, nitrate, sulphate, carbonate, diphosphate, acetate and tetraborate of sodium; the chloride, bromide, iodide, nitrate, acid sulphate, sulphate, carbonate, diacid phosphate, sulphocyanate, chromate, dichromate, ferrocyanide, acetate, benzoate and aluminium sulphate of potassium; the chloride, bromide, nitrate and sulphate of lithium; the chloride, bromide, nitrate, acid sulphate, sulphate and aluminium sulphate of ammonium; the chloride, bromide, nitrate and formate of calcium; the chloride, bromide, nitrate and acetate of strontium; the chloride, bromide nitrate, formate and acetate of barium; the chloride, bromide, nitrate, sulphate, formate and acetate of magnesium; zinc sulphate; the chloride, bromide and iodide of cadmium; the chloride, bromide, nitrate, sulphate and acetate of cobalt; the chloride, nitrate and sulphate of nickel; the chloride, nitrate and sulphate of manganese; lead nitrate; the chloride, nitrate and sulphate of aluminium; the chloride, nitrate, sulphate and acetate of chromium; copper sulphate; silver nitrate; and the chloride, nitrate, sulphate and acetate of uranyl.

A study of the data recorded in this paper will show that relations earlier pointed out[1] for other substances and temperatures hold here also. What these relations are can be seen best by collecting the data in the following tables. The volumes are 4 and 512 and the temperature coefficients are between the temperatures 50° and 65°:

Table I.—Substances with Small Hydrating Power.

	Temperature coefficients in conductivity units.	
	$V = 4.$	$V = 512.$
Ammonuim bromide	2.43	3.08
Sodium iodide	2.19	2.76
Potassium iodide	2.53	3.21
Lithium bromide	2.09	2.93
Lithium nitrate	1.78	2.55

Table II.—Substances with Large Hydrating Power.

	$V = 4.$	$V = 512.$
Calcium bromide	4.22	5.94
Calcium nitrate	4.03	5.54
Strontium bromide	3.76	5.99
Strontium nitrate	3.17	5.95
Barium nitrate	2.93	5.63
Magnesium bromide	3.81	5.83
Manganese chloride	3.03	5.81
Cobalt chloride	3.19	6.04
Cobalt bromide	3.37	5.57
Cobalt nitrate	3.11	5.33
Nickel chloride	3.20	5.45

It has been pointed out that there are several factors which contribute to the increase in the conductivity of solutions of electrolytes with rise in temperature. The diminished viscosity of the solvent with rise in temperature is undoubtedly an important factor in determining the large positive temperature coefficients of conductivity. The *decreasing mass of the ion with rise in temperature* is, however, probably a much more important factor in determining the increase in conductivity as the temperature rises—a suggestion made four years ago and which has been confirmed by all subsequent work. The solvate breaks down, becoming less complex as the temperature rises, and the mass of the moving ion, including the molecules of the solvent combined with the ion proper, becomes smaller with rise in temperature. It will consequently move faster under a constant driving force, and the conductivity will[1] therefore increase as the temperature rises.

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[1] This Journal, **35**, 445 (1906); **40**, 355 (1908); **43**, 187 (1910).

The necessary consequences of this conclusion have already been tested at lower temperatures,[2] and for a few substances at temperatures ranging from 35° to 65°.[3] The data for a much larger number of substances are now available, and we can see whether these consequences are borne out by the much larger number of facts.

The conclusions that have been drawn are:

1. Those ions with the greatest hydrating power should have the largest temperature coefficients of conductivity.

2. Substances with equal hydrating power should have approximately the same temperature coefficients of conductivity, or at least temperature coefficients of the same order of magnitude.

3. The temperature coefficients of conductivity for any given substance should be greater the higher the dilution.

The first conclusion is almost self-evident. The more complex the hydrate the greater the change in this complexity with rise in temperature. The greater the change in the mass of the ion the greater the change in its velocity with a constant driving force; consequently, the greater the change in the conductivity with rise in temperature.

A comparison of Table I with Table II will show that the above conclusion is borne out by the facts.

The conclusion that substances with equal hydrating power should have equal temperature coefficients of conductivity would be based upon the assumption that the hydrates formed by different substances would have the same degree of stability with respect to temperature, which is not true. A given ion would hold the combined water more or less firmly than an ion of another metal. We, therefore, should not expect different kinds of ions with approximately the same hydrating power to have the same temperature coefficients of conductivity. We should, however, expect them to have temperature coefficients of the same order of magnitude. If we compare the results in Table I with one another and then those in Table II with one another, we will see that each set of coefficients is of the same order of magnitude.

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[1] THIS JOURNAL, **35**, 446 (1906).

[2] *Ibid.*, **43**, 187 (1910).

[3] *Ibid.*, **35**, 448 (1906); **40**, 355 (1908).

The third conclusion is also evident: The greater the dilution the more complex the hydrate formed about the ion. The more complex the hydrate, the greater the change in the complexity with change in temperature. Therefore, the higher the dilution the larger the temperature coefficients of conductivity. If we compare the results for any substance in Table I or Table II at the two dilutions, we will find that at $V = 512$ the temperature coefficient of conductivity is always larger than at $V = 4$.

That the solvates formed by the ions decrease in complexity with rise in temperature is established by a number of lines of evidence. At the boiling points of saturated solutions the hydrates have approximately the composition of the salt with its water of crystallization. The minimum in the boiling-point curves is at a greater concentration than in the freezing-point curves, showing less complex hydrates at the higher temperatures.

The above conclusion is almost self-evidently true. Complexes in general, however great their stability, become simpler the higher the temperature. If the complexes are very stable it often requires a very considerable rise in temperature to produce an appreciable change in composition. But where the complexes are comparatively unstable, as in the case of solvates, a small rise in temperature may produce a very considerable decrease in the complexity of the system.

The necessary consequences of the solvate theory of solution are thus borne out not only qualitatively but quantitatively by the facts recorded in this paper.

The rapid increase in the conductivity of sodium carbonate with increase in dilution is due primarily to the hydrolytic action of the water. The comparatively large temperature coefficients of conductivity are also due to the increase in hydrolysis with rise in temperature. The same applies to the results with potassium carbonate.

The very high conductivities shown by potassium ferrocyanide, and the large temperature coefficients, expressed in conductivity units, are due to the large number of ions into which this salt dissociates, and to hydrolysis which increases rapidly with dilution and with temperature.

The lithium salts show smaller conductivity than the corresponding sodium, potassium and ammonium salts, due to the fact that the lithium ion is much more strongly hydrated than the other alkali ions, and this produces the well-known slow velocity of the lithium ion.

The large conductivities of salts of the alkaline earths with strong acids are due to the fact that these are strongly dissociated ternary electrolytes, and therefore yield a large number of ions in solution. The large temperature coefficients of conductivity, as has been pointed out, are due to the fact that these ions are strongly hydrated, and the hydrates decrease rapidly in complexity with rise in temperature, thus causing the velocity of the ion to increase rapidly as the temperature is raised. These salts are, of course, somewhat hydrolyzed.

The same comments apply to salts of cobalt and nickel as were made in connection with those of the alkaline earths. Hydrolysis plays an even more prominent part with the former than with the latter compounds.

When we turn to salts of aluminium and chromium we are, of course, dealing with quaternary electrolytes, or molecules that break down into four ions each. The chlorides and nitrates of the metals are also among the most strongly hydrated substances known. Further, these salts are very strongly hydrolyzed. All of these factors taken together explain the rapid increase in conductivity with dilution and the large temperature coefficients of conductivity shown by these compounds.

The conductivities and temperature coefficients of conductivity shown by the uranyl salts are just about what would be expected from the composition and nature of these salts.

Work along the lines indicated in this paper is now being pushed as rapidly as possible in this laboratory. Indeed, five investigators are now at work on the conductivities of aqueous solutions of inorganic and organic compounds at temperatures ranging from 0° to 65°.

The work is also being extended as rapidly as possible to nonaqueous solvents, and the investigations of the last ten years in this field are being supplemented by several new ones.

Physical Chemical Laboratory,
Johns Hopkins Univ.,
June, 1910.

REPORT.

THE INDUSTRIAL FIXATION OF NITROGEN.

An elaboration of a lecture on the industrial fixation of nitrogen, delivered by Professor P. A. Guye, of the University of Geneva, before the French Chemical Society was recently published in the *Bulletin*.[1] In the following pages an attempt is made to abstract those portions of Guye's article which are of special interest or not generally known. The original is a long, detailed history of the subject from the theoretical as well as the technical point of view.[2]

In speaking of the need of nitrogenous fertilizers, the author gives the following figures, quoting in part Caro and H. Erdmann:[3]

Present German Food Supply.

Crop.	Area in millions of hectares.[4]	Annual crop per hectare in kilos.	Annual crop in millions of metric tons.[5]	Annual importations in millions of tons.
Rye	6.0	1500	9.0	0.57
Wheat	2.4	1880	4.5	2.29
Oats	4.0	1720	6.9	0.97
Potatoes	3.2	12990	41.6	0.35
Barley	1.0	1660	1.7	1.62
Totals	16.6		63.7	5.80

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[1] Bull. Soc. Chim., [4] **5**, Nos. 20–21.

[2] A report on the oxidation of atmospheric nitrogen covering the theoretical work of Brode and the technical work of Birkeland and Eyde appeared in This Journal in 1906 (**35**, 358).

[3] Z. Stickstoff u. Sauerstoff Ind., 1909.

[4] 1 Hectare = 2.5 acres.

[5] 1 Metric ton = 1000 kilograms = 2204 lbs.

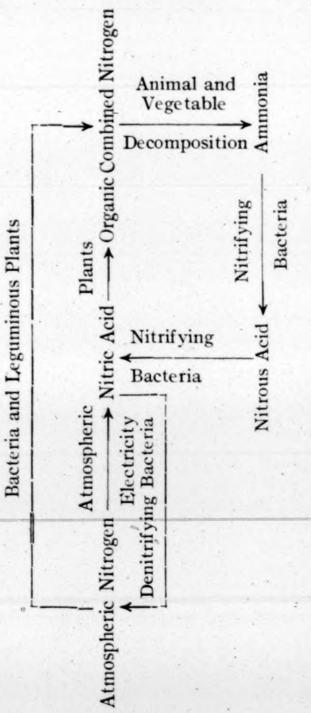
Increase in German Food Supply through Intensive Cultivation.

Crop.	Additional nitrogen required per hectare. Kilos.	Increase of crop per kilo nitrogen per hectare. Kilos.	Increase of crop per hectare in kilos.	Total increase of crop per year in millions of tons.
Rye	60	25	1,500	9.0
Wheat	130	15	2,000	4.8
Oats	100	20	2,000	8.0
Potatoes	120	100	120,000	40.0
Barley	60	25	1,500	1.5
			Total,	63.3

These figures show that Germany does not raise food enough to feed its inhabitants, but by intensive cultivation of its soil could feed a much larger population. The figures also show the need of low-priced nitrogen, and indicate a final solution of the problem of cheap bread and cheap food.

Of the fertilizing constituents in chemical fertilizers—potassium, phosphorus and nitrogen—the first two are cheap; but combined nitrogen at Fr. 1.10 to Fr. 1.50 per kilo is too dear for general use. With the drop in price, certain to come in the near future, thorough enriching of the soil will be common, and all harvests will increase enormously in amount, thus causing lower food prices. The nitrogen problem appears in this light as one of the factors of the social question.

If we examine the reserve supply of nitrogen, we find that there are about 7 metric tons of nitrogen in the air over each square meter of the earth's surface, which would suffice for 19,000,000,000 years. Supposing the earth's crust to have an average thickness of 15 kilometers, H. Erdmann considers its nitrogen content as not less than 5 tons per square meter of surface. A small portion of this nitrogen is constantly undergoing change on the earth's surface, taking part in animal and plant life. Through the action of electricity, particularly in polar regions, soluble nitrogen compounds (nitric and nitrous acids and ammonium salts) are formed in the air and fall with the rain on the soil, to be in part reduced by vegetation to free nitrogen which rejoins the air. The following table shows the cycle of nitrogen:



The coal beds and the Chili saltpeter deposits furnish the bulk of the nitrogen used for chemical and agricultural purposes. The nitrogen industry is new. At the beginning of the 19th century the only sources were the saltpeter plantations and animal excrements. The installation of gas works in 1812 and the quite recent processes for recovering the ammonia developed in coking ovens mark the beginning of industries which at present yield nearly 800,000 tons yearly.[1]

There is a steadily increasing demand for Chili saltpeter. In 1825 935 metric tons were exported; in 1860, 6800; in 1880, 226,000; in 1890, 1,065,000; and in 1908, 2,014,000. The Peruvian government, in 1888, predicted the exhaustion of the deposits in 1913; in 1900, the exhaustion was officially postponed to 1940; and in 1907 again postponed to 2032. These changes are chiefly due to discoveries of new deposits, in part to improved methods of working the old deposits. While the supply is sufficient for the present, the price will rise rather than fall, as the richer deposits are exhausted and the poorer require more labor and fuel per ton of nitrate. Despite the demand, the industry is far from prosperous at present nitrate prices.

When we look to the coal beds for nitrogen, we find that the recent advances in this field are due to the work of Dr. Ludwig Mond, which began in 1879. At that time there were numerous patented processes for obtaining ammonia from air by conducting air mixed with steam over heated porous material, preferably glowing coke. Mond proved that in any one of these processes the amount of ammonia obtained was the same whether air were admitted or not, and that the nitrogen of the ammonia obtained came solely from the coke. Mond's own process consists in making generator gas at as low temperatures as possible, thus avoiding certain decompositions and obtaining most of the nitrogen in the coal as ammonia. About two tons of water per ton of coal are mingled with air and introduced into the generator. The resulting gas contains 60–70 per cent. of the nitrogen of the coal in the form of ammonia, which is absorbed by sulphuric acid; the gas is used as fuel under the name of "Mond gas." The best method of using this or any other generator gas is to burn it in gas engines.

Within the last few years the Mond system has been successfully applied to poor lignite and wet peat. Poor lignite deposits and peat bogs are yielding ammonium sulphate and electrical energy.[2]

Methods for the production of synthetic ammonia by the action of electric discharges on a mixture of nitrogen and hydrogen, or by decomposition of metallic nitrides, with subsequent regeneration of the nitride, are not as yet of commercial value. The electric discharge tends to decompose the ammonia at temperatures below that of formation, and similar difficulties are encountered with the nitrides. The author thinks that it is probable that the hindrances to these methods may be overcome. The raw material is at hand. Hydrogen may at need be extracted from water gas; it is obtained as unused by-product in the electrolytic production of sodium hydroxide; the hydrogen now wasted would, however, yield only 39,000 tons of ammonium sulphate yearly. Nitrogen may be obtained at relatively low price by fractioning liquid air, for—even considering the oxygen as dead loss—the nitrogen costs only 0.2 to 1 cent per kilo. As a kilo of ammoniacal nitrogen is worth 40 cents, and as it is of great advantage to the nitric acid industry to work with air very rich in oxygen, we shall see in the future processes such as the synthetic preparation of ammonia or cyanamide worked by the side of processes for synthetic nitric acid.

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[1] H. Erdmann estimates the production of ammonium sulphate for 1907 at 778,400 metric tons, of which Great Britain produced 310,000, Germany 260,000, and the United States only 60,000, despite the fact that 40,770,000 tons of coke were made in the United States in 1907.

[2] Frank and Caro say of their adaptation of the Mond process to wet peat that the electrical energy (from dynamos driven by gas engines burning the Mond gas) is clear profit, as the ammonium sulphate pays working expenses and interest on capital.

There are two successful methods of transforming ammonia into nitric acid. The first is by lowering the oxidation temperature of the ammonia by suitable catalyzers, completing the oxidation at temperatures below that at which ammonia decomposes. A German establishment by this method obtains from coking-oven ammonia two tons of 88 per cent. nitric acid per 100 tons of coal. The second method of oxidation is that of Professor Muntz, in Paris, who utilizes the bacteria of peat bogs for this purpose. The oxidizing power of these bacteria seems to be so enormous that if synthetic ammonia could be obtained in sufficient quantity at low price we should have a complete solution of the nitrogen problem.

Calcium cyanamide is made by the well-known process of Frank and Caro, which consists in fixing nitrogen by calcium carbide, thus converting it into the cyanamide, $CaCN_2$, and is so well known that it is only necessary to recall the advantage of combining its manufacture with that of nitric acid, using the excess nitrogen for the first and equal volumes of nitrogen and oxygen for the second.

In all processes for oxidizing atmospheric nitrogen by electrical energy the action is really thermal. Air is acted on by the heat generated by the electric arc in special furnaces; some of the atmospheric nitrogen combines with some of the oxygen of the air, forming nitric oxide, which, after leaving the furnace, is converted by atmospheric oxygen into nitrogen dioxide; to transform the nitrogen dioxide into salable products, the air containing these nitrous vapors is submitted to various processes, the simplest of which is the action of water or of bases, yielding nitric acid or a mixture of nitrate and nitrite.

That the electric spark brings about the formation of oxides of nitrogen in the air was shown by Priestley in 1785 and by Cavendish in 1788. Perrot, in 1861, obtained the same results with the Ruhmkorff coil (mixture of sparks and small arcs) and was the first to show that prolonged discharges produce a greater amount of nitric acid than short discharges. Berthelot, in 1870, showed that the electric arc produces the same chemical effects as the spark, but with greater intensity. As the work of Rayleigh, of Dougal and Howles, of Kowalski and Moscicki, the earlier work of Guye and Naville, and the processes of Bradley and Lovejoy and Birkeland and Eyde were so fully described in THIS JOURNAL,[1] Guye's descriptions may be omitted.

In studying the three types of furnace in actual use, we see that in the Birkeland-Eyde system a moving arc is employed, the magnetic field acting as motive force. In the processes of the Badische Aniline and Soda Company and of Guye a quiet arc is used. Guye thinks that at the working temperatures (2500°–4000°) of the great arc furnaces, the speed of the gaseous molecules is so great, and their mixture by diffusion so rapid, that it is practically superfluous to hasten the mixing process by the sweeping action of the moving arc. The one essential condition is that the interior of the oxidation chamber shall be practically filled by the arc.

The Badische Company's furnace, as described by Schönherr,[2] has a practically motionless arc in the axis of the long,

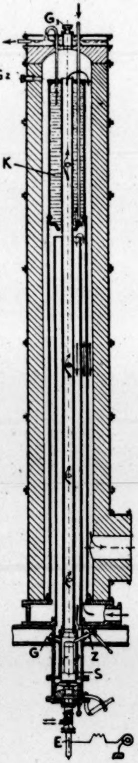

Fig. 1.

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[1] THIS JOURNAL, **35**, 358. To make the present article clear, it may be said that the principle of the Birkeland furnace is to force a rapid current of air across a flame disc at high temperature, causing the oxidation of a part of the nitrogen. The flame disc in a 500 kilowatt furnace is two meters in diameter and is formed by the action of the magnetic field on the arc. The yield from a furnace of this size is 500 kilos nitric acid per 10-hour day.

[2] Electrotech. Z., **1909**, Nos. 16, 17. Witt: Chem. Ind., **28**, 609.

narrow, vertical oxidation chamber. The essentials of this furnace (Fig. I) are a central metallic tube, the upper part of which is cooled by water circulation, and a lower electrode, *E*, also cooled by water. The points of attachment of the arc are the head of the electrode *E* and the upper water-cooled part of the furnace. The top of the arc can be observed through the openings G_2 and G_3, the lower part through the opening *G*. The circulation of the air is shown by the arrows. By passing twice around the central tube, the air is heated to 500°, and enters the tube at the base through an opening placed tangentially to the axis. According to Schönherr, this causes a rotating movement of the air in the central tube, the arc being the motionless axis of this air spiral; and the length and stability of the arc depend upon the rotary motion of the air.[1]

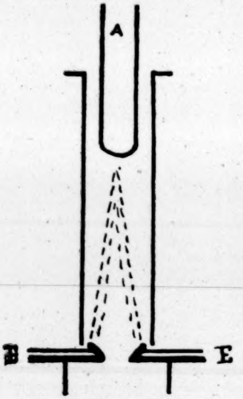

Fig. II.

Schönherr claims as advantages of the Badische Company's furnace, as compared with the Birkeland furnace, greater simplicity and economy, as it does not require the fragile and costly apparatus for forming a magnetic field. The arc—which for a 600 h. p. (442 kilowatts) furnace is 5 meters long—glows quietly in the axis of the furnace and requires little care; it is rarely extinguished and is easy to re-establish. The yield is said to be better than that of the Birkeland furnace.

Guye then describes his own furnace. He uses an arc playing between two electrodes at the base of a vertical tube; air enters the tube at the base. The upward draught in the tube elongates the arc into the form of an inverted V, as shown in Fig. II. Guye's furnace is shown diagrammatically in Fig.

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[1] Guye says that his experiments show that the arc remains nearly as constant in the center of the tube if the air enters freely the lower open end of a vertical tube, the tube forming one electrode, a terminal below the lower opening the other. In this case rotation is impossible. He ascribes the great stability of these arcs to the fact that gas viscosity increases with the temperature: for nitrogen, at —191° $\eta = 0.324$; at +300°, $\eta = 1.6279$; that is, in an interval of 500°, the ratio of increase in viscosity is 1: 5.

III. Five vertical tubular chimneys, *C, C*, stand in a chamber, into which air enters through the openings *O, O*. The air may be heated by circulating about the tubes. The electrodes *E* are in electric tension. The stability of this system of several arcs is much greater than that of a single arc of the same tension, each arc serving as autoregulator to its neighbor. The sum of the lengths of the arcs is much greater for a given current than in any other furnace. In his furnace of 50 kilowatts power working at a tension of 5,000 volts with 5 arcs, the sum of the length of the arcs is between 5 and 6 meters. The Badische Company's 442 kilowatt furnace working at 4,200 volts with nearly nine times the power produces an arc of five meters in length.

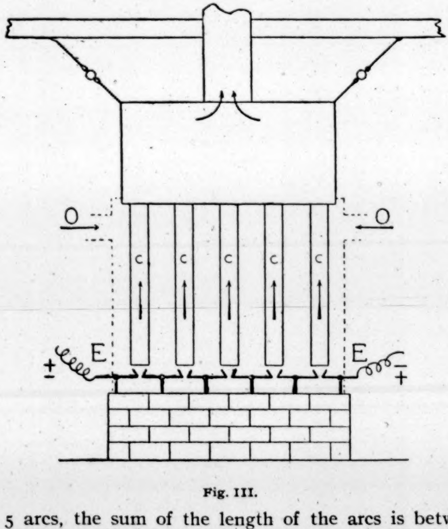

Fig. III.

The tubular chimneys are narrow enough to be completely filled by the arc. A cooler may be put above the arc *A* (Fig. II) to ensure more rapid cooling of the gases, at the moment of their leaving the zone of oxidation, without cooling the electrodes. A little experimental furnace of this kind ran day and night for 6,000 hours; for some months it ran every night without attendance. The 50 kilowatt furnace has been running at Geneva for over half a year with satisfactory results; in the roughly constructed furnace without preliminary heating of air and without cooling apparatus, the yield is 545 to 560 kilos nitric acid per kilowatt year. The 2 kilowatt experimental furnace yielded 350–390 kilos per kilowatt year. This increase of yield with increase of power conforms to theory and leads Guye to expect a much higher yield in his new 500 kilowatt furnaces now in course of construction at Geneva.

In the processes now in use, only 3 per cent. of the total energy employed is utilized in the oxidation of nitrogen. Improvements suggested by the author are as follows:

1. The use of dried air. Nitrate of lime would probably be the best drying agent, as it is readily dehydrated again by waste heat.

2. Compression of the nitrous vapor before entering the absorption apparatus.

3. The partly de-oxygenated air leaving the absorption apparatus should not be allowed to re-enter the furnace.

4. A mixture of air and oxygen should be substituted for air.

5. Work under reduced pressure (about 100 mm.) in the oxidation chamber increases yield.

By adopting some of the features enumerated the author thinks the yield can be increased to 1000 kilos per kilowatt year.

In all of these processes for making nitric acid, the gases on leaving the furnace are utilized to heat steam boilers. The temperature of the gases entering the boiler tubes is about 700°; that of the gas leaving the tubes about 250°–300°. At these temperatures the tubes are scarcely injured by the gases, which then pass into the re-oxidation tower, cooling tower, and finally enter the absorption apparatus at temperatures below 100°. The absorbing agents are water or sulphuric acid or basic solutions.

When air traverses a furnace and absorbers the following stages may be distinguished:

Stage a. Air is rapidly heated to 3000° or higher. Above 1500° nitric oxide, NO, is formed.

1. $\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftarrows NO$ (—21.6 Cal.).
2. $N + O \rightleftarrows NO$ (? Cal.).

When the air contains moisture—ordinary air always does—it is possible that a small quantity of nitric oxide is formed by the following reaction:

3. $\frac{1}{2}N_2 + H_2O \rightleftarrows NO + H_2$ (—79.7 Cal.).

At the same time most of the water vapor dissociates.

4. $H_2O \rightleftarrows H_2 + \frac{1}{2}O_2$ (—58.1 Cal.).

The free hydrogen and oxygen could react in two opposite ways, either lessening the content of nitric oxide through the reducing action of the hydrogen, or increasing it through the increase in oxygen concentration. The author's experiments show that increase of water vapor in the air means a decrease in production of nitric oxide and lead him to consider the reducing effect predominant.

Stage b. The first cooling from the temperature of the arc to about 1200° causes the reversion of nitric oxide to nitrogen and oxygen if the cooling is not instantaneous; this reversion is never entirely avoided.

Stage c. The second period of cooling extends from 1000° to 500°–600°. Apparently no important chemical transformations occur in this stage.

Stage d. The third period of cooling begins at 500°–600° and reaches to ordinary temperatures. It is marked by the different oxidation equilibria of nitric oxide into the oxides, which may occur in different ways; either by successive oxidation: $NO \longrightarrow N_2O_3 \longrightarrow NO_2 \longrightarrow N_2O_4$ (Berthelot, Raschig); or by a direct oxidation: $NO \longrightarrow NO_2$ with ulterior formation of N_2O_3 by addition of NO to NO_2 (Lunge, Engler). The first view is generally accepted; probably both are correct and both reactions simultaneous. Whatever the interpretation, the important fact is that with air containing 1–2 per cent. of nitric oxide, at ordinary temperatures, a final equilibrium results between the gases present; this certainly occurs between nitric oxide and nitrogen peroxide, probably nitrogen trioxide is also in the mixture. The presence of the oxide N_2O_4 is admitted by all workers; that of nitric oxide and nitrogen peroxide the author has proved by isolating these gases. The relative proportions of the oxides NO_2, N_2O_4, N_2O_3 and NO will vary with the concentration of combined nitrogen. In dilutions of about 1 per cent. oxides of nitrogen, the free nitric oxide forms 10–20 per cent. of these oxides; 0.9 of the remainder is nitrogen peroxide, NO_2, and 0.1 is the oxide N_2O_4 with a little trioxide.

The dilution of the oxides of nitrogen in practical work, and their equilibrium, explain the great difficulty found in absorbing these oxides completely by water or even by sulphuric acid.

In the cooled furnace gases, nitrogen peroxide predominates; a small part is present as N_2O_4, which reacts with alkali or water, a fresh quantity forming from the peroxide NO_2. The reaction with water is: (*a*) $N_2O_4 + H_2O = NO_3H + NO_2H$; (*b*) $3NO_2H = NO_3H + H_2O + 2NO$. As the nitric oxide formed in reaction (*b*) is re-oxidized, all oxides would be finally changed to nitric acid were it not for the conditions of equilibrium referred to above; and further, as the concentration of the unabsorbed oxides diminishes a point is reached where the oxide N_2O_4 becomes unstable and dissociates into the peroxide NO_2. From this point the further absorption is in the form of nitrous acid. (*c*) $NO_2 + NO + H_2O = 2NO_2H$, or (*d*) $N_2O_3 + H_2O = 2NO_2H$. This nitrous acid then decomposes according to reaction (*b*). It can be calculated that if the absorption follows the cycle *a—b*, the gases must run through this cycle four times to absorb 99 per cent. of the oxides of nitrogen; but if it follows the cycle *c–b* or *d–b*, it must run through nine times to reach the same result.

These last considerations show why if an absorption by water is followed by an absorption by alkali the yield from the alkali absorption is principally nitrite. It is true, however, that some of the nitrite is formed by the reaction discovered by Gay-Lussac and studied by Sabatier: $4NO + 2NaOH = N_2O + 2NaNO_2 + H_2O$.

Industrially 40 per cent. nitric acid is obtainable by water absorption, even from very dilute gases.

If nitrite is desired it is better to conduct the furnace gases over alkali while still at a temperature of 300°. This is the principle of the Badische Company's nitrite process.

The concentration of the acid is best carried out by using calcium nitrate as dehydrating agent; two successive treatments with this brings the 40 per cent. acid to 95 per cent. without loss of nitrous fumes.

Coignet has patented a process to substitute nitric for sulphuric acid in the manufacture of superphosphate:

$$Ca_3(PO_4)_2 + 4HNO_3 = 2Ca(NO_3)_2 + Ca(H_2PO_4)_2.$$

By conducting the furnace gases over calcium phosphate, the salts $Ca(NO_3)_2$, $Ca(NO_2)_2$ and $Ca(H_2PO_4)_2$ are formed. This mixture would be an excellent fertilizer.

It has been proposed to isolate the oxide N_2O_4 by cooling the furnace gases to low temperatures; considering the great dilution, it would be necessary to cool the whole mass of gas to -100° to separate all the compound N_2O_4. Sir William Ramsay has patented a process for combining this cooling with the liquefaction of air and separation of oxygen from nitrogen, his purpose being to treat a mixture of equal volumes of the two gases in the oxidation furnace.

Guye has shown experimentally that the impure oxide N_2O_4 can be purified by passing oxygen through it, and that its transformation into the oxide N_2O_3, by adding nitric oxide, takes place smoothly. Further, the dried liquids, N_2O_3 and N_2O_4, do not act on metal containers. Hence the industrial transportation and use of these liquefied gases presents no more difficulty than that of chlorine or phosgene.

If the oxide N_2O_4 could be marketed at low price, it might effect a revolution in the manufacture of explosives, as mixtures of it with various organic compounds yield high-power explosives which, as yet, have been little studied.

We all know that it is necessary, in changing alkali chlorides to nitrates, to evaporate repeatedly with nitric acid in excess, and that the escaping gases are a mixture of unchanged hydrochloric acid, of chlorine and of oxides of nitrogen. Therefore, there is as yet no industrial production of sodium nitrate by this reaction. Guye says that he will soon publish details of a method by which a quantitative yield of hydrochloric acid and sodium nitrate can be obtained by this reaction. So synthetic Chili saltpeter may yet be brought on the market. Calcium chloride may be changed to calcium nitrate by the same method, thus closing the last gap in the cycle of the Solvay process by marketing the worthless calcium chloride as calcium nitrate and hydrochloric acid.

Methods of employing the energy wasted in the furnace processes will doubtless be developed in the future. At present a furnace absorbing 1000 kilowatts energy and producing 500 tons nitric acid yearly, develops during the same period as much heat energy as is developed by burning 1000 tons of coal, while according to Schönherr only 30 per cent. of this enrgy is utilized in making steam;[1] yet this 30 per cent. is equivalent to 300 tons of coal for each 500 tons of acid.

E. Renouf.

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[1] Schönherr says of the Badische Company's furnace, that 3 per cent. of the energy is used in forming nitric acid, 40 per cent. is absorbed in cooling the gases before entering the boilers, 17 per cent. is lost by radiation, 30 per cent. is recovered by the boilers, and 10 per cent. is lost by the cooling after the gases leave the boilers.

OBITUARIES.

GEORGE FREDERICK BARKER.

George Frederick Barker, a past president of the American Chemical Society and of the American Association for the Advancement of Science, was born in Charlestown, Massachusetts, July 14, 1835, and died at Philadelphia, May 10, 1910. His early education was obtained in the public schools of Boston and at the academy of South Berwick, Maine. He next served an apprenticeship with Joseph Wightman, a well-known maker of scientific instruments in Boston, from whom he received a mechanical training which served him in good stead in later years. The ability to construct his own apparatus was gained in those early days. With this preparation he entered the Sheffield Scientific School, from which he graduated in 1858 as Bachelor of Philosophy. From 1859 to 1861 he was an assistant in the Harvard Medical School, then Professor of Chemistry in Wheaton College, Illinois, and afterwards in the Albany Medical College, which gave him his degree of M.D. In 1863 he taught in the University of Pittsburgh, and in 1868 and 1869 he delivered lectures on chemistry in Williams College. In 1869 he was appointed Professor of Physiological Chemistry and Toxicology in the Yale Medical School, going thence, in 1872, to the chair of Physics in the University of Pennsylvania, where the remainder of his scientific career was spent. In 1900 he was made Emeritus Professor, but that did not imply any cessation of his real activity. His contributions to science continued till within a few years of his death.

In his scientific work Professor Barker was peculiarly versatile. On the one hand he was intensely interested in purely theoretical questions, as may be seen from the most casual inspection of his text-book on "Elementary Chemistry." He often gave to American audiences their first hearing of new advances in theoretical chemistry, and in doing so he displayed to a remarkable degree the gift of clearness. On the other hand, much of his attention was devoted to technical subjects, the application of science to human welfare. As a court expert he was much in demand, and was most successful. Theory and practice, to him, went hand in hand as inseparable partners. His keen critical faculty was a source of strength to him in both fields of his activity.

In strictly original investigation, Professor Barker's output was not large. In his younger days, problems of organic and physiological chemistry occupied much of his attention. Later, as Professor of Physics, his mind turned more to electrical questions. His adaptability to widely dissimilar conditions is thus clearly shown. In which field of work he appeared to the best advantage it would be difficult to say. During the later years of his life he was much interested in radioactivity, and studied especially the radioactivity of thorium minerals,

Apart from his duties as a teacher, Professor Barker found time for other occupations. For some years he served on the Board of Education of Philadelphia. He was in charge of the spectroscopic work of an expedition made to observe the total solar eclipse of 1878. In 1881 he was United States Commissioner to the Electrical Exhibition at Paris, and vice-president of the Jury of Awards. In recognition of this service, France made him a "Commander" in the Legion of Honor. He also served as juror at the Chicago Exposition of 1893.

Professor Barker was president of the American Association for the Advancement of Science in 1879, and of the American Chemical Society in 1891. He was also a member of the National Academy of Sciences, an officer of the American Philosophical Society, a corresponding member of the British Association, and honorary member of the Royal Institution. Honorary degrees were given him by the University of Pennsylvania, Allegheny College, and McGill University.

On the social side, Professor Barker was a delightful companion. He enjoyed attending scientific gatherings, and meeting his coworkers in the advancement of knowledge. There was nothing of the pedant or recluse in his character. His presence will be much missed in the various organizations to which he belonged.

F. W. CLARKE.

HEINRICH CARO.

Hofrath Dr. Heinrich Caro, known to chemists as the former scientific head of the Badische Anilin- und Soda-Fabrik, died Sept. 11th, aged 76.

Caro was born in Posen in 1834. He studied in the Posen Gymnasium and in the University and Gewerbe-Schule of Berlin; in the latter institution he was a pupil of the young Professor Adolph von Baeyer. Caro became interested in color chemistry and devoted himself to technical work first in Mühlheim in 1855, then in Manchester in 1859, where he was in the employ of Roberts, Dale & Co., subsequently becoming a member of the firm. Two German chemists of high attainment in color chemistry were then residing in England, A. W. Hofmann and Peter Gries; Caro was in touch with them and with W. H. Perkin, and the friendship and influence of these three men were a spur to the talented young chemist. A new method for making mauveine, the discovery of the alcohol-soluble blue indulines, and the Manchester yellow patented by Dale, Martius and himself, were among the results of his stay in England. In 1866 he returned to Germany, going to Heidelberg and intending to devote himself to pure chemistry. In 1868, however, he was offered the position of technical manager and head chemist of the Badische Anilin- und Soda-Fabrik; he accepted this position and remained in active service with this company until 1890, and was connected with it in an advisory capacity till the time of his death. The constant and rapid development of this firm from its comparatively small importance at its start to the vast field of industry covered by its present activity is largely due—perhaps chiefly due—to Caro's ability in chemical research and his remarkable power of guiding and inspiring each and every one of his host of young coworkers in carrying out their several investigations. Space is lacking to mention the discoveries in new dyestuffs made by Caro with the help of the constantly growing army of young chemists—all picked men, mostly university graduates with the doctor's degree—who are in the employ of this great establishment. Caro's lecture before the German Chemical Society, in 1891, published in the *Berichte* of that year, gives an idea of their number and importance.

In addition to Caro's grasping and controlling the chemical work of the factory he found time for purely scientific investigations. Witness his papers with Graebe and Liebermann on synthetic alizarin, with Graebe on rosolic acid, rosaniline and acridine, with Baeyer on oxyanthraquinones, nitrosodiphenylaniline and nitrosophenol.

Caro took a leading part in the improvement of the patent laws in Germany and in most of the prominent movements for the encouragement and regulation of chemical industry.

On Caro's retirement from active participation in the work of the factory in 1890, he did not cease his chemical work but continued it in his own laboratory; perhaps the most striking result of the work of this period was his discovery of the "Sulfomonopersauere," better known as Caro's acid.

Caro's personality was attractive; he was quiet and reserved, much beloved by his friends, coworkers and all who had the privilege of knowing him.

E. R.

ZDENKO HANS SKRAUP.

Prof. Zdenko Hans Skraup, known to all chemists for his work on the quinic alkaloids and for the synthesis of quinoline which bears his name, died suddenly on Sept. 10th.

Prof. Skraup was born in Prague on March 3, 1850. His early education was received in the schools of his native city and in 1871, after one year's military service, he became assistant to Prof. H. L. Buff in the Prague Technical High School, from which he had just graduated. Shortly after he took up technical work and for a time was employed in a porcelain and stoneware factory and later in the Vienna mint. In 1873, however, following his bent for scientific research, he accepted an assistantship in the University of Vienna under Prof. Rochleder, at whose suggestion he began a study of the oxidation of cinchonine, his first step on a road he was to follow so long and with so much success. After Rochleder's death, in 1874, Skraup remained with his successor, Lieben, and for a time his work on the alkaloids was interrupted. In 1875 he obtained his doctor's degree at Giessen. While with Lieben, he studied the iron-cyanogen compounds, but soon resumed his investigations of cinchonine and related compounds, and although again called to the field in 1878 with the army of occupation in Bosnia, where he so distinguished himself that he was given a decoration and promoted to a first lieutenancy, he was able, within the next 15 years, to shed much light on this problem, and his work has contributed largely towards establishing the constitution of the quinic alkaloids. It was during this period that he discovered his famous quinoline synthesis (1880).

In 1881 he became professor of chemistry at the Vienna "Handelsakademie." Six years later he succeeded Maly at the Technical High School in Graz and the following year he accepted a professorship at the university in the same city, which he held until 1906, when finally, on a second call, he went to the University of Vienna. While in Graz he continued his investigations on the alkaloids, but his activity was by no means limited to this field, as is shown by his work on maleic and fumaric acids, the discovery of the formation of a new biose in the hydrolysis of cellulose, the preparation of lead tetrachloride, and the extensive study of albumens which he began in 1904.

Skraup was a member of many scientific societies and vice-president of the Deutsche Chemische Gesellschaft. He was cut off in the fulness of his activity, and by his death chemistry suffers an inestimable loss.

REVIEWS.

The Simple Carbohydrates and the Glucosides. By E. Frankland Armstrong, D.Sc., Ph.D., Associate of the City and Guilds of London Institute. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1910. pp. ix + 112.

This treatise is one of the series of "Monographs on Biochemistry" edited by R. H. Aders Plimmer and F. G. Hopkins. It is highly recommended to chemists interested in carbohydrates and enzymes. There are seven chapters dealing with the pentoses, hexoses, disaccharides, the relation between configuration and properties, hydrolysis and synthesis, and the natural and synthetical glucosides. The bibliography is very full. The book does not give a complete account of the sugars, but furnishes rather a summary of the more recent advances to those already familiar with the carbohydrates.

The treatment of the relation between configuration and enzyme action is excellent, much of Armstrong's own work in this field helping to illuminate the subject. There are some loose statements: On page 9 it is stated that "when glucose is prepared by artificial means, a mixture in equal proportions of *d-* and *l-*forms is actually obtained." The author surely does not stop to think that *d-*glucose is made *artificially* from *d-*mannose or *d-*fructose without the simultaneous production of *l-*glucose. In some other similar cases, however, the actual facts are clear from the context.

This book and that of Bayliss on "The Nature of Enzyme Action" together give an excellent account of some of the actions of amyloclastic and proteoclastic enzymes.

S. F. Acree.

Die Sprengstoffe, ihre Chemie und Technologie. Von Dr. Rudolf Biedermann, Geheimer Reg.-Rat und Professor der Chemie an der Universität Berlin. 286 Bändchen. Aus Natur und Geisteswelt, Sammlung wissenschäftlich-gemeinverständlicher Darstellungen. Mit 15 Figuren im Text. Leipzig: Druck und Verlag von B. G. Teubner. 1909. pp. iv + 128. Price, M. 1.25.

This work, like its companions in the "Aus Natur und Geisteswelt" series, is in the convenient form of a pocket edition and it demonstrates that, through the careful selection of material, the exercise of a sound sense of proportion, and the use of concise but clear methods of expression, a large amount of valuable information may be compressed into a small space and yet be in a convenient form for use. The subject matter is divided into three chapters: The historical development of the invention of explosives, the theory of explosives, and the technology of explosives. Under the second chapter there are presented in sufficient detail to serve as a useful introduction for beginners or as a reminder to those skilled in the art, the subjects of the energy of explosives, their thermochemistry, comparative efficiency, reaction equations, gaseous volumes, velocity of decomposition, initial impulse, explosion temperatures, explosion pressures, and density of loading. In the third chapter is given a sufficient number of typical examples of explosives to illustrate all the various classes. The book contains several illustrations, a large number of tables of data, and frequent references to literature. It is brought up to the date of publication and is sound and trustworthy. CHARLES E. MUNROE.

THE MECHANICAL APPLIANCES OF THE CHEMICAL AND METALLURGICAL INDUSTRIES. A Complete Description of the Machines and Apparatus used in Chemical and Metallurgical Processes for Chemists, Metallurgists, Engineers, Manufacturers, Superintendents and Students. By OSKAR NAGEL, PH.D., Consulting Chemical Engineer. With 292 Illustrations. Second Edition. New York: Published by the Author, P. O. Box 385. 1909. pp. vii + 307.

This book, following on somewhat similar lines the well-known work of Parnicke, is intended, according to the author's statement in the preface, "to clear up ideas regarding the mechanical appliances used in the chemical and metallurgical industries, to expose the real importance of the machines used in the various processes and to get rid of the obscurities prevailing at present in these matters." The reader of the book soon experiences a feeling that the author has not entirely succeeded in all his aims. Many of the machines and appliances are accorded very meagre treatment, while the frequent omission of index letters or numbers from the diagrams and text render the descriptions far from clear; as, for example, the inadequate consideration of the topics of Magnetic Separation, of Steam Pumps, of Crushing Rolls and Jaw Crushers. Even the excellent diagram of the Positive Pressure Blower, Fig. 120, hardly warrants dismissing the subject with the statement: "The working of this machine is so simple and so well known that a detailed description is not necessary." Probably most engineers and superintendents would understand the working of this machine from the diagram alone, but nontechnically trained chemists, manufacturers and students may not. Complicated diagrams, such as Figs. 43 and 97, without index lettering, are of little service in elucidating the text. Throughout the book there is considerable verbiage and repetition.

But overlooking these defects, there really is much useful information for the nontechnical reader, and the engineer may find something here and there in the work. The chapters on Steam and Water, Electric Power, Gas Power, Purification of Gases, Firing and Furnaces, Drying Appliances and Separating, are well done. A short chapter on Temperature Measurements closes the book proper; in the appendix is a paper by the late Mr. Oscar Guttmann on "The Works Chemist as Engineer," read before the Society of Chemical Industry. The mechanical make-up of the book is very good; the type is very legible and the illustrations are generally clear and sharp. A few misprints have crept in, notably on p. 36 (time for tank), p. 42 (retort for retard), and p. 153 (sulphuric for sulphurous). F. H. THORP.

THEORETICAL PRINCIPLES OF THE METHODS OF ANALYTICAL CHEMISTRY BASED UPON CHEMICAL REACTIONS. By M. G. CHESNEAU, Ingenieur en Chef des Mines, Professeur d'Analyse Minérale à l'École National des Mines. Authorized translation by AZARIAH THOMAS LINCOLN, PH.D., Assistant Professor of Chemistry, Rensselaer Polytechnic Institute, and DAVID HOBART CARNAHAM, PH.D., Associate Professor of Romance Languages, University of Illinois. New York: The Macmillan Co. 1910. pp. x + 184. Price, $1.75.

The author has classified and discussed theoretically a number of analytical operations in an interesting way, and has made rather free use of mathematical formulas in his treatment of the subject. Perhaps the most novel feature of the work is the use of a "calorimetric" method of explaining the phenomena of solutions, instead of the employment of the ionic theory as a basis. To the reviewer, the method adopted seems far less satisfactory than the one which Ostwald has made so well known in a book upon the same subject. However, the author of the present work devotes a chapter to the electrolytic theory of double decomposition of salts, and another chapter to objections to the theory, so that fully one-quarter of the book is devoted to a discussion of the view which he has not adopted. These chapters may be useful to those who are interested in the controversial aspect of the ionic theory.

Although one of the translators is a professor of Romance Languages, it appears that a slip has been made here and there in the rendering of the French into English. For instance, on page 172, sulphuric and oxalic acids are designated as being *rare*, whereas the evident intention is to say that they are *exceptional* in a certain behavior. The book has the inconvenient lack of an alphabetical index, as is frequently the case with books of French origin. H. L. WELLS.

DIE BESTIMMUNGSMETHODEN DES WISMUTS und seine Trennung von den anderen Elementen. Von PRIVATDOZENT DR. L. MOSER, Technische Hochschule Wien. Die Chemische Analyse. Sammlung von Einzeldarstellungen auf dem Gebiete der chemischen, technisch-chemischen und physikalisch-chemischen Analyse. Herausgegeben von DR. B. M. MARGOSCHES, Privatdozent an der Deutschen Technischen Hochschule, Brünn. Stuttgart: Verlag von Ferdinand Enke. 1909. pp. 126. Price, M. 4.

The purpose of this book, as outlined in the preface, is to present as complete an account as possible of the analytical chemistry of bismuth, and to collect information which may be of value in future research in this field. Many analytical processes are accordingly described which are of historical or chemical interest, but which are of little value in accurate analytical work. For this reason, however, and on account of the author's successful treatment of the subject, the book will undoubtedly have a wider circle of readers than would a mere description of a few reliable methods of analysis.

In the introduction of fifteen pages the author considers briefly the general chemistry of bismuth, including its history, occurrence, and preparation from the ores. Qualitative tests and separations are dealt with in ten pages; and the remainder of the book is devoted to quantitative methods of analysis under the following heads: (I) gravimetric, 18 pp.; (II) volumetric, 11 pp.; (III) colometric, 1 p.; (IV) gasometric, 1 p.; (V) electroanalytical, 9 pp.; (VI) separations, 25 pp.; and (VII) analysis of special substances, 16 pp.

The last section of the book will prove of especial value to the practical analyst, since it deals with the problems most frequently encountered in actual work, *viz.*, analyses of the crude metal, ores, alloys, and pharmaceutical products. The usefulness of the book is also increased by the fact that the author's experience in this field has enabled him to judge of the value of many of the methods. He considers the gravimetric determination of bismuth as phosphate to be the best method of analysis and points out the sources of error in many other methods. W. C. BRAY.

POST'S CHEMISCH-TECHNISCHE ANALYSE. Zweiter Band. Viertes Heft. Dritte vermehrte und verbesserte Auflage, herausgegeben von PROF. DR. BERNHARDT NEUMANN, Grossherzogliche Technische Hochschule Darmstadt. Mit zahlreich eingedruckten Abbildungen. Braunschweig: Vieweg und Sohn. 1909. pp. xiv + 467. Price, M. 12.

This part of the latest edition of Post's well-known handbook of the methods of chemico-technical analysis is devoted to coal tar, the mineral pigments, the natural and synthetic dyestuffs, and the color lakes. Except for a few paragraphs carried over from the edition of 1890, these chapters have been entirely rewritten with the addition of so much new matter that the number of printed pages is increased about fourfold. The fact that the work of compilation was entrusted to the hands of Professor Gustav Schultz, of Munich, is in itself a guarantee that the material used has been judiciously selected and arranged. The volume will be found a valuable work of reference by all who are interested in the manufacture, use, or analysis of colors. S. P. MULLIKEN.

TOXIKOLOGISCHE CHEMIE. Von DR. E. MANNHEIM. Privatdozent für pharmazeutische Chemie an der Universität Bonn. Mit 6 Abbildungen. Sammlung Göschen. No. 465. Leipzig: G. I. Göschen'sche Verlagsbuchhandlung. pp. 150. Price, M. 0.80.

A booklet of 150 pages, representing one of a series of very elementary writings on the various branches of chemical science published under the name of "Sammlung Göschen." Being written very clearly it answers the purpose of acquainting the reader with the fundamental principles of practical Toxicology. As a book of reference or for any detailed study it is naturally not suitable. C. V.

AUSFÜHRLICHES LEHRBUCH DER PHARMAZEUTISCHEN CHEMIE. Bearbeitet von DR. ERNST SCHMIDT, Geh. Regierungerat, o. Professor der pharmazeutisch-chemischen Instituts der Universitat Marburg. Mit 95 eingedruckten Abbildungen. Zweiter Band. Organische Chemie. Fünfte vermehrte Auflage. Erste Abtheilung. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1910. S. xvi + 1020. Preis, geheftet, M. 23; geb., M. 25.50.

The author in this part of his extensive work on Pharmaceutical Chemistry considers those chemical substances of the aliphatic series that are important to the pharmacist. In the introduction we find a well-outlined discussion of the relationship of the various groups of organic compounds in regard to constitution and properties. Analytical methods are described in detail. The customary classification of organic chemistry is adopted. Illustrations of chemical apparatus are freely inserted. For those chemicals used in Pharmacy the Latin names of the Pharmacopea are adopted beside the purely chemical nomenclature. The occurrence in nature of the organic substances and their isolation and preparation are well described. The book is up-to-date and thoroughly scientific. One objection may be raised in regard to the absence of references to the more important original papers. This represents one, although perhaps the only, deficiency of this system. C. V.